STUDIES ON THE CHEMICAL CONSTITUTION, PROPERTIES AND USES OF BASIC SLAGS.

A THESIS

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INTRODUCTION WITH OUTLINE OF STUDIES.

Basic slag may be defined as a product obtained in the manufacture of steel from pig-iron containing more phosphorus than is required.

The presence of phosphorus in steel, except in very small amounts, renders it brittle and unsuitable for many manufacturing purposes. Highly phosphatic iron ores are consequently unsuitable for the manufacture of pig-iron for steel making, unless the phosphorus can be removed in the smelting. Attempts to remove the phosphorus from the iron ore in the blast furnace have been unsuccessful on account of the highly reducing conditions which are necessary for the recovery of the iron from the ore, existing there. Experiments by Snelus in 1872, and by Thomas and Gilchrist in 1878 demonstrated the possibility of removing the phosphorus from molten pig-iron by treatment in a Bessemer converter. This consisted of blowing air through a charge of molten pig-iron with added lime, in a converter lined with dolomite. A series of exothermic reactions are thus set up, resulting in the removal of silicon, phosphorus, manganese, and other associated "metalloids" from the pig-iron

and the formation of a slag containing a large percentage of calcium.

The basic Bessemer process suffered from certain disadvantages which caused it to be replaced to a very great extent in Great Britain by the basic open hearth process.

Essentially the difference between these refining methods is in the method of oxidation of the materials associated with the iron in the pig-iron. In the Bessemer process direct oxidation is obtained by the passage of air through the charge: whereas in the open hearth process, about seventy per cent. of the oxidation results from the action of oxide of iron on the "metalloids". The remainder is due to the oxidising gases of the furnace.

In the basic open hearth process the operations consist of charging lime, scrap and pig-iron on to a basic hearth heated from above by superheated producer gas. Initially there is surface oxidation. As the charge melts the oxide comes into contact with the oxidisable "metalloids", and these are to some extent oxidised.

The order in which the "metalloids" are oxidised in the open hearth process differs from that of the Bessemer

in a manner which has an important influence on the quality or grade (amount of phosphoric oxide present) of the slag produced. In the basic Bessemer process the phosphorus is oxidised and enters the slag at the end of the process, being the last of the "metalloids" to be removed from the iron into the slag. The richness of the latter in phosphoric oxide depends on the original content of phosphorus in the pig-iron. For the basic Bessemer process the pig-iron should contain about 2 per cent. phosphorus, for the basic open hearth treatment .5 - 1.5 per cent. phosphorus content is preferable: if over 1.5 the steel refining process is prolonged.

In the basic open hearth process the silica and phosphorus are removed together and it is possible to obtain a high grade slag by interrupting the refining when the phosphorus content of the metal bath is about .2%. In ordinary practice, however, due to other considerations, this is not done, and the slag is run off when the steel bath is ready to be tapped. If the pig-iron contains much sulphur, a larger quantity of lime is required. As lime is added the slag thickens and reaches a viscosity

which slows the progress of the "boil". This may be corrected by the addition of oxide of iron in the form of mill scale, to give fluidity. Such treatment tends to increase the phosphorus and sulphur in the bath. The only treatment found to give the required result in such a case is addition of fluorspar.

Thus Basic Slags obtained from steel manufacture may be classified into two groups depending on the process employed - (1) Basic Bessemer slags,

(2) Basic open hearth slags.

The former group generally containing 16 - 18 per cent. phosphoric oxide (P_2O_5) have been proved to be valuable fertilisers when finely milled, and may be termed a bye-product.

The percentage phosphoric oxide content in basic open hearth slags varies from about .5% to over 15%. Those under 8% are considered, by the manufacturers, not worth grinding for use as fertilisers, but may be used for other purposes. The others of this group, according to the Citric Acid solubility test are sub-divided into two classes (1) of high solubility, (2) of low solubility. Where fluorspar has been added to the steel furnace the second

class of basic slags is usually produced. These are commonly referred to as "Fluorspar" Slags. Both of these classes are ground for use as fertilisers.

The importance of Basic Slags as fertilisers may be judged from the quantities delivered for use in Great Britain, 1912-32.

	Tons.
Year ending September 30, 1912.	290,000
" " " " 1920.	440,000
" " " " 1921.	248,000
" " " " 1922.	247,000
" " " " 1923.	278,000
" " " " 1924.	286,000
" " May 31, 1925.	243,540
" " " " 1926.	261,160
" " " " 1927.	162,480
" " " " 1928.	158,640
" " " " 1929.	321,800
" " " " 1930.	305,750
" " " " 1931.	215,330
" " " " 1932.	152,940

For 1930, the consumption of Superphosphate in Great

Britain and Ireland was 664,000 tons: the imports of Mineral Rock Phosphate into the United Kingdom and Irish Free State were 496,000 tons.

An important distinction between Basic Slag and other fertilisers is that the amount available is dependent on the demand for steel. (A point worthy of note in regard to this is a statement, appearing in a Memorandum by British Basic Slag, Ltd. to 6th Report of the Basic Slag Committee of the Ministry of Agriculture and Fisheries to the effect that "sufficient slag can be produced by the British Steel Makers to supply the whole requirements of the country".)

Moreover, since Basic Slag is a product of relative unimportance, when compared with steel, to the steel maker, it does not "carry much weight" when changes in methods of manufacture of steel are involved. These changes may, however, make important differences in the slag produced. Such was found to be so when during the Great War, 1914-18, the Bessemer process was superseded by the open hearth method of dephosphorisation in steel manufacture. Variations in the working of the open hearth process, as already indicated, produce further differences, so that in place of basic

Bessemer slag, which had been definitely established by experiments such as the well known Cockle Park trials begun by Sir Wm. Sommerville and continued by Sir Thomas Middleton and D. A. Gilchrist, as a valuable fertiliser, there appeared the open hearth slags whose value had to be assessed.

Following preliminary work on these, in 1920 the Faraday Society held a discussion on "Basic Slags - their production and utilisation in Agriculture". This led to the appointment by Lord Lee, Minister of Agriculture of a Basic Slag Committee, whose terms of reference were "To consider the development and improvement of the manufacture of basic slag and the extension of its use". Ten reports, containing a large amount of valuable information about the fertilising properties of basic slag have been issued.

About 1928 attempts were made to reduce the fluorine content of low soluble slags, with a view to increasing the solubility.

The object of this research was to study the chemical constitution and properties of basic slags as produced after 1928, especially those to which fluorspar had been added in small quantities, and to compare the fertilising value of a high citric acid soluble and a low

citric acid soluble slag.

The results obtained are given in two sections. Part 1 deals with the constitution and chemical properties. Part 2 deals with the results obtained in field trials on grass land and arable land.

A summary of the previous literature relative to each section is given at the beginning of each part.

PART 1.

Summary of previous Literature.

A. Carnot and A. Richard (Compt. Rend., 1883, 97, 316. Bull. Soc. Fr. Min. 1883, 6, 237) examined some prismatic, blue crystals from basic slag. They found them to consist of a mixture of calcium phosphate and silicate.

G. Hilgenstock (Stahl und Eisen 1883, 3, 498) isolated brown orthorhombic plates and found them to have the composition 4 Cao.P_2O_5.

Two types of crystals similar to the above-mentioned were noted by A. von Groddeck and K. Broockmann (Stahl und Eisen, 1884, 4, 141), but failing to detect silica in the blue crystals they reported them both as tetracalcium phosphate.

E. Jensch (Ber. 1886, 19, 3093) stated that the most important compounds in basic slag were calcium silico phosphate,

tetracalcium phosphate, and calcium ferrite.

J. T. Stead, C. H. Ridsdale, and H. A. Miers (Journ. Iron and Steel Inst. 1887, 1, 222; J. Chem. Soc. 1887, 52, 601) isolated several types of crystals from a basic Bessemer Slag. These were examined microscopically and chemically. The minerals separated were (1) Tetracalciumphosphate. This occurred in fairly large rectangular crystals, which were transparent, of faint yellow colour, slightly pleochroic, and apparently belonging to the orthorhombic system.

(2) Calcium silico phosphate. This formed blue well developed crystals belonging to the orthorhombic system. They were markedly pleochroic.

(3) The third type, on chemical analysis, appeared to be tetracalcium phosphate, containing about 10% impurity, mainly ferric silicate. These crystals apparently belonged to the hexagonal system. They gave a hexagonal cross-section showing pyramidal cleavage, and were markedly dichroic, the colour varying from light to dark brown.

(4) "Feathery" crystals, which on analysis proved to be composed of ferrous and ferric oxides, lime, and magnesia.

(5) Two varieties of "black spear shaped crystals which

resembled flakes of graphite", one of which was attracted by a magnet. Each consisted chiefly of lime, ferric oxide, and alumina, with about 8% ferrous oxide present in the magnetic material.

H. Bucking and G. Linck (Stahl und Eisen 1887, 7, 557) made an examination of similar material. They verified the orthorhombic nature of tetra calcium phosphate. The blue silico phosphate, approximately of composition 4 $Ca_3P_2O_8$, 3 Ca_3SiO_5 (with ferrous iron replacing part of the calcium) was found to belong to the monoclinic system. A third type of crystal of composition approximately 4 $Ca_3P_2O_8$, Ca_3SiO_5, belonging to the hexagonal system was found. The optical properties were similar to those of the hexagonal compound described by Stead and Ridsdale. In cooling from high temperatures, the rhombic tabular crystals separate first, then the hexagonal type, and finally the blue monoclinic material.

The conclusions of Bucking and Linck were combatted by G. Hilgenstock (Stahl und Eisen, 1887, 7, 557: 1889, 9, 498) who maintained that the various crystals were different forms of tetracalcium phosphate, with the silica present as an impurity.

G. Forster (Zeit. angew. Chem. 1892, 5, 13) prepared an analogue of fluorapatite with the formula $3\ Ca_3\ P_2O_8\ CaO$ and stated that this is found in the residue when basic slag is treated with citric acid.

Further crystallographic details of tetracalcium phosphate were given in 1895 by Termier and Richard (Bull. Soc. Min. 1895, 18, 391).

The same year, A. Carnot (Ann. Mines. 1895, 8, 300) reviewed the whole question of the nature of the compounds found in basic slag, and maintained the individuality of the silico phosphates described by Stead and himself.

C. G. T. Morison (J. Agr. Sci. 1909, 3, 161) suggested that the phosphorus compound in basic slag was a silico phosphate having approximate composition Feo. 5 CaO. P_2O_5. SiO_2. He concludes that free lime and calcium present as carbonate does not exceed 7½% and discusses the action of calcium compounds on the solubility of phosphorus compounds present in a solution of carbon dioxide.

J. Hendrick (J. Soc. Chem. Ind. 1909, 28, 775: 1911, 30, 520) showed by chemical tests that a considerable amount of the "lime" present in basic slags is capable of acting as a base.

The nature of the calcium compounds was however not determined.

V. A. Kroll (Stahl und Eisen, 1908, 28, 675: Journ. Iron Steel Inst. 1911, ii, 126) published a discussion on previous work with an account of his own investigations. He stated that another silico phosphate approximately 6 CaO P_2O_5 2 CaO SiO_2 was the chief constituent of Thomas slag and that the two silico phosphates previously described had been formed from this during slow cooling. This silico phosphate is described as occurring in the form of greenish blue hexagonal crystals. Further optical data is however not given. He also mentions the occurrence of compounds of the spinel group, and of free oxides.

G. Hilgenstock (Stahl und Eisen, 1909, 29, 1478) however still maintained that the silico phosphate should be separated into a phosphate and a silicate, tetrabasicity of the former being maintained.

About this time H. Blome (Stahl und Eisen, 1910, 30, 2161 Metallurgic 1910, 7, 659 and 698) examined the system calcium phosphate (4 CaO P_2O_5) calcium silicate (2 CaO SiO_2) and found two maxima on the melting point curve corresponding

to (1) 4 CaO P_2O_5 2 CaO SiO_2

(11) 4 CaO P_2O_5 4 (CaO SiO_2)

This work was criticised by Hartleb (Zeit. off Chem. 1911, 17, 381: 1912, 18, 221) who stated that the occurrence of tetracalcium phosphate in basic slag was rare.

E. Steinweg (Zeit. Geo. Hutt. 1912, 9, 28) investigated the influence of cooling on the relative proportions of the phosphate and silico phosphate, and confirmed Kroll's observation that slow cooling favoured the formation of silico phosphates.

O. Nielsen (Ferrum. 1913, 10, 97) has investigated in part the system CaO SiO_2 P_2O_5. He found maxima at points represented by Ca_3 P_2O_8 and Ca_3 P_2O_8 3 SiO_2. No optical data was given.

M. Popp and co-workers (J. Landw., Ver. Stat. 1913, 79, 229) agreed with the conclusions of Stead and Carnot.

S. H. Collins and A. A. Hall (J. Soc. Chem. Ind. 1915, 34) concluded that the citric solubility of slags is correlated with the constituents of slags in such a manner that it may form a useful test provided that its arbitrary and conventional character is recognised.

G. S. Robertson (J. Soc. Chem. Ind. 1916, 35, 216) showed

that the properties of basic slag are modified by the addition of fluorspar to the melt; "the phosphate or phosphates which such a slag contains do not appear to be in combination with silica and they seem to bear a very close resemblance to those contained in mineral phosphate". The official citric acid test showed low solubility of the phosphate which was completely soluble if the extraction was repeated sufficiently.

H. Bassett (J. Chem. Soc. 1917, iii, 620) in a study of the phosphates of calcium found no evidence of the existence of tetracalcium phosphate but he obtained what he regarded as hydroxy apatite with a fairly extensive region of stability. He states that of all the calcium phosphates this is the only one not decomposed by water, and it can dissolve unchanged but the saturated solution is extremely dilute.

A. A. Ramsay (J. Agr. Sci. 1917, 8, 277) found that addition of calcium carbonate to tricalcium phosphate reduced the percentage solubility figure of the phosphoric oxide. He stated that "2% citric acid is more correctly a solvent for lime than for phosphoric acid", and from his experiments concluded that the manurial value of phosphates cannot be determined by a 2% citric acid solvent.

F. Bainbridge (Trans. Faraday Soc. 1921, 16, 302) identified fluorapatite, in slags to which fluorspar had been added, both by analysis and micro-examination. The composition of the magnetic material in the slag was similar to that of the "feathery" crystals described by Stead and Ridsdale.

N. Sheldon (Trans. Faraday Soc. 1921, 16, 310) examined fluorspar slags. He found the two above-mentioned types of crystals present, together with yellow-brown hexagonal and small angular fragments of another substance. Bainbridge suggested that the former is the phosphate and the latter calcium orthosilicate.

A. Scott and D.N. McArthur (J. West Scotland Iron and Steel Inst. 1922, 29, 79) published detailed results of microscopic examination of basic open hearth and basic Bessemer slags. Polished and etched specimens were examined by reflected light, and thin sections in transmitted light. Chemical analyses of the slags and their molecular formulae are given. Non-fluorspar slags were found to consist essentially of three types of compounds - silico phosphates, spinelloid compounds and free oxides. Three silico phosphates were found present in the slags examined, although never more than two co-existing in one slag.

(1) The brown crystals described by Stead and Ridsdale with ratio SiO_2 : P_2O_5 = 1 : 4.

(2) The pleochroic crystals described by Stead and Ridsdale, the SiO_2 : P_2O_5 ratio being unity.

(3) A new silico phosphate first described by the authors whose SiO_2 : P_2O_5 ratio is 3 : 1. This compound occurs as colourless or practically colourless non pleochroic crystals with optical properties approximating to the blue silico phosphate.

With fluorspar slags a decidedly different equilibrium was noted. The calcium fluoride had combined with the phosphate to give fluorapatite. The silica was present as dicalcium silicate.

No evidence was obtained to show that the introduction of fluorspar caused the equilibrium between the spinelloid material and the free oxides to differ from that obtained in the non-fluorspar slags.

J. F. Tocher (J. Agr. Sci. 1922, 12, 125) in a study of the citric acid solubility of mineral phosphates concluded that "citric solubility, if applied to fertilisers, may in a certain degree be a measure (1) of fineness of grinding as

already pointed out by other workers, but it seems necessary also to postulate similarity of composition in comparing degrees of fineness in practice; (2) of the presence or absence of alkaline substances in fertilisers approximately of the same composition and ground to the same degree of fineness; (3) of the presence or absence of fluorides as well as alkaline substances in slags; and (4) of the differences in the constitution of the phosphatic compounds in finely ground fertilisers containing approximately the same proportions of extraneous substances".

G. S. Robertson and F. Dickinson (J. Soc. Chem. Ind. 1923, 42, 59, 1) while realising the empirical nature of citric acid solubility suggested a modified citric acid test as a means of obtaining a rough value of insoluble phosphatic fertilisers.

H. F. L. Bischoff and B. de C. Marchand (J. S. African Chem. Inst. 1923, 6, 53) in determining citric soluble P_2O_5 in basic slag found that variations in time of shaking, type of shaker, and volume of solution can be made without much influence on the result. Fine grinding of the sample previous to determining the solubility, of bone and rock

phosphates, in citric acid had a marked effect on the amount of phosphoric oxide dissolved.

E. Vanstone (J. Agr. Sci. 1925, 15, 36) investigated the relationship between phosphate soluble in 2% citric acid and total phosphate in the case of phosphates of known composition, basic slags and mineral phosphates. He concluded that in the case of three slags of different citric solubility that the citric solubility is constant independent of the sample weight used in the test, "when allowance is made for a small constant error in the determination" and stated that "the Wagner test is not so empirical as usually supposed".

Vanstone's figures for the citric solubility of the three basic slags with percentage citric solubility calculated are given below.

"Table 111 p.39.

Citric solubility of basic slags.

Weight taken. (gm.)	No. 1 P_2O_5 present (gm.)	No. 1 soluble. (gm.)	No. 2. P_2O_5 present (gm.)	No. 2. soluble. (gm.)	No. 3. P_2O_5 present (gm.)	No. 3. soluble (gm.)
1	.1749	.1674	.1032	.0703	.0849	.0520
3	.5247	.4674	.3096	.1633	.2547	.0970
5	.8745	.7642	.516	.2645	.4245	.1493
8	* 1.0494	.9126	.8256	.4073	.6792	.2247 "

* 6 gm. here

Percentage citric solubility of P_2O_5.

	No. 1.	No. 2.	No. 3.
1	95.7	68.1	61.2
3	89.1	52.7	38.1
5	87.4	51.3	35.2
8	87.0	49.3	33.1

In another paper (J. Agr. Sci. 1925, 15, 491) Vanstone proposed the use of 2% oxalic acid solution to eliminate the effect of soluble calcium in evaluating basic slags and mineral phosphates.

The chemistry of basic slags formed the subject matter of another paper by the same author (J. Agr. Sci. 1927, 17, 143). He treated two slags, differing in solubility and phosphate content, for long periods with a boiling solution of ammonium chloride, and found that the low grade slag lost about 70% of the total lime and very little phosphoric acid. The slag residue was thus considerably enriched in phosphate content. The high soluble high grade slag also lost a large percentage of the total lime but large amounts of phosphoric acid were also found in solution. He concluded from solubility experiments that a silico phosphate was

present in the high soluble slag but not in the low grade low soluble slag. The citric acid solubility of the residues after treatment with ammonium chloride was determined. The view that fluorspar slags contain the phosphate as fluorapatite was confirmed.

T. Dunkel (Stahl und Eisen 1927, 47, 1205) found that the rate of cooling of converter slag, i.e. Thomasslag, without influence on the citric acid solubility, which could be increased by addition of certain quantities of silica to give a fixed SiO_2 : P_2O_5 ratio.

A. Sullwald (Stahl und Eisen 1928, 48, 547) found that under ordinary conditions the rate of cooling had no influence on the citric solubility of slags. Rapid quenching or granulation in water however decreased the solubility. When basic slag was cooled in large blocks the total and citric soluble phosphoric acid increased regularly from the outside to the middle.

S. Smeja (Przemysl. Chem. 1928, 12, 137) indicated that the final equilibrium of reaction between citric acid and tricalcium phosphate depends on fineness, temperature, time of action and quantity of water present.

H. Weiss (Archw., Eisenhuttenw. 1928. 2, 81) investigated

factors influencing solubility of Thomas slags. He found that the influence of cooling on solubility was slight and that the unfavourable influence of hardness of some slags on solubility was largely mechanical.

H. Schneiderhohn (Mitt. Kaiser Wilhelm Inst. Eisen forsch Dusseldorf, 1928, 10, 213 - Cf.C.A. 1929, p. 2679) dealing with Thomas slags examined three different states of cooling with and without additions of silica. The microscopic recognisable constituents were ascertained and noted, and the structure and texture of the individual samples described and explained. Tempering experiments showed that no decomposition occurred, and that the existing parts of the mixture were conceived as states of equilibrium depending on the concentration of the substances concerned. Only the grain size was increased by the tempering. To establish the nature of the constituents of the mixture solubility experiments were conducted and the soluble constituents analysed. Silico carnotite, 5 CaO P_2O_5 SiO_2, crystallised oxide of calcium, magnesium, iron, and aluminium, and in samples without added silica hilgenstockite 4 CaO P_2O_5 were indicated. As the cause of the unequal citric solubility of the slags with and without silicic acid added

was recognised first of all the soluble calcium compounds, which repress the solubility of the silico carnotite, while the dissimilar ions going into solution in the sample with addition increased the solubility of the silico carnotite. Attention is directed to the neutralising value of slags and to the estimation of effective lime content.

From the change in reaction of an acid soil by the admixture of basic slag - C. Brioux and E. Jouis (Compt. Rend. 1929, 189, 117) estimated the active "lime" content to be more than 30%.

E. J. Janitzsky (iron Age 1929, 124, 1235) gave report of chemical analyses, colour, conformation and texture of spoon samples of slag from twenty basic open hearth steel heats.

J. Kuusk (Acta. Commentationes Univ. Tartuensis 1930, 20A, 1) studied the optimum conditions for formation of citric soluble phosphate by heating natural phosphates, of fluorapatite structure, with silica. The presence of more than 10% of ferric oxide and alumina lowered the citric solubility of the phosphate. Kuusk thought that the citric soluble phosphoric oxide is present as a silico phosphate. $3\,Ca_3(PO_4)_2CaSiO_3$ which resulted from the replacement by SiO_2 of the fluorine in the fluorapatite compound: the fluorine

being volatilised as silicon tetrafluoride.

A. Wilhelmij (Z. Pflan 2 Düng 1931, 19A, 129) gave a detailed account of the solubilities and fertiliser values of a large series of typical German basic slags. They are all of the high soluble type by the citric acid test, and no mention is made of the low soluble type which until the last few years formed about half of the British production (in 1931-32 the low soluble total was 41,243 tons). As much as 70-80% of the total phosphoric oxide in the German slags tested by Wilhelmij was soluble provided the extractions were repeated sufficiently. The rate of dissolution varied considerably but was greatest in slags with much soluble silica, as determined by extraction with a 5% solution of sodium carbonate. The essential component is believed by Wilhelmij to be a double salt of tetracalcium phosphate and calcium metasilicate, which breaks up in water and undergoes further decomposition to give dicalcium phosphate and calcium hydroxide. The solubility and availability of the phosphoric acid in slag is considered to depend on the amount of lime and silica present and on the rate of decomposition of the double salt, and this in turn on the rate of cooling of the slag. Modern slags are reckoned to be cooled more quickly and are

more readily soluble than the old ones in most of the recorded experiments.

Different views from those of Wilhelmj are put forward by H. Schneiderhohn (Arch. Eisenhuttenw. 1931, 5, 9) who states that tetracalcium phosphate is a less common and less soluble compound than silico carnotite and is formed only when the silica content is less than 5 CaO : 1 P_2O_5 : 1 SiO_2. He also showed that addition of fluorspar to give 1% F. in the slag may reduce the citric solubility from more than 90% to about 4%.

EXAMINATION OF TWO BASIC OPEN HEARTH SLAGS AS SUPPLIED FOR FERTILISER. (NOV. 1930).

No. 1. No fluorspar had been added to the steel bath.

No. 2. Fluorspar had been added during the dephosphorisation process.

Other details of manufacture, and lump samples of the ball slag, i.e. before grinding, for preparation of sections for microscopic examination were not obtainable.

Table No. 1. Chemical compositions.

	Slag 1.	Slag 2.
% CaO	43.99	49.18
% P_2O_5	12.55	10.71
% SiO_2	11.00	14.30
% MgO	7.00	5.90
% FeO	9.20	3.70
% Fe_2O_3	4.70	5.28
% MnO	7.10	6.60
% Al_2O_3	1.10	2.70
% S	0.20	0.26

Table No. 2 Molecular Concentrations.

	Slag 1.	Slag 2.
CaO	.785	.877
P_2O_5	.0883	.0754
SiO_2	.182	.237
MgO.	.174	.146
FeO	.128	.0515
Fe_2O_3	.0294	.0331
MnO	.100	.0931
Al_2O_3	.0108	.0265

The molecular formulae expressed according to the method of Scott and McArthur (1):-

Slag 1.

CaO .785, MgO .174, MnO .100, FeO .128) Fe_2O_3 .0294, Al_2O_3 .0108) SiO_2 .182, P_2O_5 .088

i.e. RO : .0339 R_2O_3 : SiO_2 .155, P_2O_5 .0748

Slag 2.

CaO .877, MgO .146, MnO .093, FeO .0515) Fe_2O_3 .0331, Al_2O_3 .0265) SiO_2 .237, P_2O_5 .0754

i.e. RO : R_2O_3 .051 : SiO_2 .203, P_2O_5 .0646

Attempts to separate some of the important constituents of these slags, by making use of differences in the physical properties such as density, magnetic attraction, and hardness as exhibited in power of resistance to grinding, of the component compounds were tried out on small samples. A heavy liquid separation using bromoform, as in common geological practice, proved unsatisfactory in both cases due to the formation of aggregates. This unfavourable effect due to particle sizewas further demonstrated in an attempted separation with the electro magnet. No separation was obtained with the samples used.

Separation of the slags into five fractions, according to particle size, by sieving was carried out.

Fractions.

(1) refusing to pass sieve with 100 meshes to the linear inch (official sieve for testing fineness of basic slags).

(2) passing 100 mesh sieve, but refusing sieve of 120 meshes to the linear inch.

(3) passing 100 and 120 sieves, but refusing 150 mesh sieve.

(4) passing 100, 120, and 150 sieves, but refusing 200.

(5) passing through all four sieves.

The amount of each fraction obtained from a given sample was noted, and determination of "CaO" and "P_2O_5" content was carried out on each fraction, to find if concentration of

the components of high resistance power to grinding in the coarser fractions, and vice-versa, concentration of these of low resistance power to the finer fractions, with consequent differences in chemical composition had been obtained.

Table No. 3.

Slag 1.

Fraction	%	% CaO	% P_2O_5
1	13.9	42.60	11.70
2	8.8	42.81	12.12
3	35.2	42.54	12.50
4	27.0	46.00	12.64
5	15.1	45.92	13.55

Slag 2.

1	23.5	49.40	10.90
2	40.2	48.67	10.80
3	24.1	50.12	10.54
4	6.8	48.88	10.43
5	5.4	48.53	10.30

The molecular ratios CaO : P_2O_5 from these results for each fraction are given in the following table.

Table No. 4 CaO : P_2O_5 ratios.

Slag 1.

Fraction	CaO : P_2O_5		
1	.760 : .0823	=	9.2 : 1
2	.764 : .0853	=	8.95 : 1
3	.759 : .0880	=	8.63 : 1
4	.821 : .0890	=	9.22 : 1
5	.819 : .0954	=	8.59 : 1

Slag 2.

1	.881 : .0767	=	11.49 : 1
2	.868 : .0760	=	11.42 : 1
3	.894 : .0742	=	12.05 : 1
4	.872 : .0734	=	11.88 : 1
5	.866 : .0725	=	11.94 : 1

Discussion of Results.

Slag 1. The fineness of this sample according to the official method is 86%. Slight variations in composition of the various fractions are noted, with increasing content of phosphoric oxide as particle size diminishes. The "CaO" figures do not increase consistently with diminution of particle size and consequently slight variations in the

molecular ratio CaO : P_2O_5 for the different fractions are obtained.

The increased concentration of P_2O_5 in the finer fractions probably indicates that the phosphorus compound or compounds present in the slag have less resistant power to grinding than some of the other components of the slag. The CaO : P_2O_5 ratio figures show slight variation but give no definite evidence as to whether one or more phosphorus compounds are present.

Slag 2. The fineness of this sample 76.5% is not up to the official requirement. The "CaO" and "P_2O_5" content figures for the various fractions show very little variation and consequently no distinct concentration has been obtained.

Solubility Tests with fractions separated.

Stead (2) has shown that citric acid solubility of basic slags was associated with the fineness. Increased fineness with low soluble slags gave higher phosphate solubility in citric acid. In a study of solubility of mineral phosphates Tocher (3), as already noted (p. 16) has remarked on the effect of fineness on citric acid solubility: Bischoff and Marchand have also noted increased solubility of bone and rock phosphates with fine grinding.

The five fractions of the two slags in question have been examined in this respect.

The solubility of the "CaO" and "P_2O_5" in 2% citric acid solution according to the official method were determined. i.e. 5 gm. in 500 c.c of 2% citric acid solution, contained in a litre shaking bottle, are shaken in an end-over-end shaker, at 30 revs. per. min., for 30 minutes.

The solubility of the "P_2O_5" was also determined by the method proposed by Wanstone (4). The quantities used being similar in amount to those for citric acid solubility.

NOTE:- In above mentioned and other solubility tests in this work the constituents found in solution immediately after shaking period has terminated and the solid residue has been separated are reported as soluble. This is remarked on, since it does not take into account the possibility of reprecipitation, as solid, of material that has been dissolved.

Table No. 5 2% Citric Acid Solubilities.

Slag No. 1	Citric Acid Extract.			
Fraction	CaO		P_2O_5	
	% soluble	% solubility	% soluble	%solubility.
1	34.45	80.8	10.60	90.6
2	42.15	98.5	11.53	94.8
3	42.50	99.9	12.47	99.9
4	43.40	94.4	12.34	97.6
5	41.01	89.3	12.81	94.5
Slag No. 2				
1	25.80	52.2	1.90	17.3
2	29.10	59.8	2.41	22.4
3	29.80	59.6	2.44	23.2
4	27.34	54.9	2.69	25.8
5	19.98	41.2	2.70	26.2

The molecular ratios soluble "CaO" : "P_2O_5" are given the following table.

Table No. 6. Molecular ratios of citric acid soluble CaO:P_2O_5

Slag 1.

Fraction	CaO	:	P_2O_5			
1	.615	:	.0746	=	8.24	: 1
2	.752	:	.0811	=	9.27	: 1
3	.758	:	.0877	=	8.64	: 1
4	.7741	:	.0868	=	8.91	: 1
5	.731	:	.0901	=	8.12	: 1

Slag 2.

1	.460	:	.0134	=	34.42	: 1
2	.519	:	.0170	=	30.54	: 1
3	.532	:	.0172	=	30.95	: 1
4	.488	:	.0189	=	25.75	: 1
5	.357	:	.019	=	18.76	: 1

Discussion of results.

The non-fluorspar slag shows high solubility both of CaO and P_2O_5, and the molecular ratios of soluble CaO : soluble P_2O_5 are practically the same as in the solid material, in close proximity to that required for the 3 : 1 silico phosphate (1). Consideration of the molecular formula for the slag shows that there is not sufficient silica present

to give all the phosphorus in the form of the 3 : 1 silico phosphate. The 1 : 1 silico phosphate is probably present also. Increasing solubility with fineness is obtained in this case only with fractions 1, 2, 3, thereafter a diminution results. With the fluorspar slag fractions increasing solubility with fineness as noted by Stead (2) is obtained. The CaO : P_2O_5 ratios in the citric acid extracts are widely different from these of the slag fractions, indicating that one of these is combined to an appreciable extent with some other constituent of the slag. The compounds concerned are probably dicalcium silicate and apatite as found in fluorspar slags by Bainbridge (5) and McArthur (6).

Consideration of the molecular ratios CaO : P_2O_5 of the residue shows that these are approaching that of apatite, but that there still remains dicalcium silicate to be dissolved. The CaO : P_2O_5 ratios are given in Table No. 7.

Table No. 7 Molecular ratios of citric acid residues.

Slag 2.

Fraction	undissolved CaO : P_2O_5				
1	.421 : .0633	=	6.65	:	1
2	.349 : .0570	=	5.91	:	1
3	.362 : .0570	=	6.36	:	1
4	.384 : .0545	=	7.05	:	1
5	.509 : .0535	=	9.52	:	1

Oxalic Acid Solubility.

Vanstone (4) proposed the use of oxalic acid in testing the solubility of phosphatic fertilisers. He assumed that the solvent in the soil is carbonic acid and since oxalic acid resembles it more closely in chemical constitution and chemical properties than citric acid particularly in forming an insoluble calcium salt, its use is to be preferred in testing the solubility of phosphatic fertilisers. The solubility of the phosphate contained in the fractions separated from the two slags was determined using quantities similar in amount to those used for the citric acid solubility tests. The results are tabulated below.

Table No. 8. Oxalic Acid Solubility.

Fraction	% Soluble P_2O_5	% Solubility
Slag 1.		
1	1.92	16.4
2	2.80	23.1
3	3.25	32.7
4	5.12	40.5
5	5.60	41.3
Slag 2.		
1	.645	5.92
2	2.42	22.36
3	2.68	25.05
4	3.64	34.90
5	3.23	31.36

Discussion of results.

Percentage solubility of P_2O_5 in non fluorspar slag fractions is in every case much lower than that obtained with citric acid treatment: while the increase with fineness is progressive.

This increasing solubility with fineness is also obtained with the fluorspar slag fraction, and it is interesting to note that solubility in 2% oxalic acid exceeds that in 2% citric acid in fractions 3, 4, 5. The variation in solubility in 2% oxalic acid with difference in fineness of grinding is greater than that shown with 2% citric acid under the conditions of the test.

Microscopic examination of Slag 2.

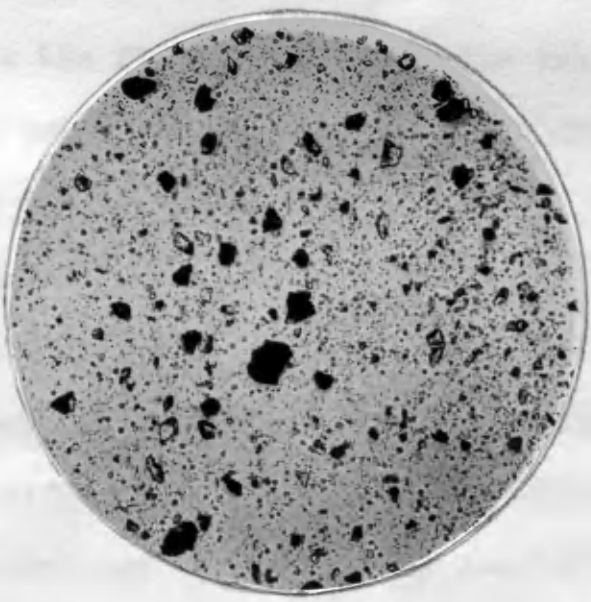
Although ball samples of this slag were not obtainable for preparation of sections for examination according to the methods of Scott and McArthur (1), slides of the various fractions, with the powder embedded in canada balsam were prepared. Fractions No. 2 or 3 are most suitable for this purpose.

Identification of minerals in such slides is a more difficult matter than in those prepared from the ball slag, due to interference and diffraction colours developing.

Furthermore the approximate relative amounts of the compounds cannot be judged so well as in thin sections.

The presence of large amounts of transparent material with high refractive index and low double refraction was noted. The optical properties of this material indicate apatite, as suggested from the solubility tests.

The following micro photograph of fraction 2 of slag 2 shows the presence of the colourless material of high refractive index.



Solubility of "P_2O_5" of fluorspar slag 2 on repeated extraction with 2% citric acid.

G. S. Robertson (7) has shown that the phosphate in fluorspar slags which he examined is soluble in 2% citric acid solution if the extraction is repeated. He does not give full details of the methods used. A difficulty arises in the case of repeated treatments in the recovery of the residue after the first extraction, if as in the official method the suspension obtained after shaking is filtered through a large filter paper to give a quick separation of the solution from the residue, unless the filter paper with the residue unwashed or washed with hot water or other suitable reagent is transferred to the shaking bottle. If this process is repeated several times the accumulation of filter paper would not be helpful to quick filtration. Filtration under pressure might be employed instead of the above method, but here the same difficulties would be encountered.

To overcome the difficulty smaller quantities of the requisite materials were used, and instead of filtering, the suspension was centrifuged at high speed, the supernatant liquid thereafter being poured off. Centrifuge tubes, 100 cc. capacity, with well fitting rubber

stoppers were used to take the place of the shaking bottles. The quantities of slag and 2% citric acid solution employed for the test were .8 gm. and 80 cc. respectively to each tube. Two of the tubes, with the ends fitted with the stoppers together can then be placed in the ordinary end-over-end shaker, and shaken for the required period. The suspension after such treatment is centrifuged at high speed, and the clear liquid poured off. The required time for a good separation is not more than 3 minutes. From 80 cc. of the solution used 79.5 can easily be recovered for analysis. The usual procedure was to use four tubes with the required quantities. These are shaken and centrifuged together, and the solutions, after pouring, bulked.

The soluble phosphate obtained with repeated extraction, by this procedure, was determined in the fluorspar slag used in the foregoing experiments. Soluble "CaO" was not determined, but the acidity of the extract was ascertained by titration with standard alkali.

Table No.8.

Repeated extraction of fluorspar slag with 2% citric acid solution, .8 gm. in 80 cc., shaken for 30 minutes at 30 rev/min.

No. of extract	% Sol. "P_2O_5"	Acidity
1	2.32	100 cc ≡ 16.9 cc N Alkali
2	2.27	100 cc ≡ 26.55 " "
3	2.25	100 cc ≡ 27.7 " "
4	1.89	100 cc ≡ 28.25 " "
5	1.80	100 cc ≡ 28.3 " "

Total soluble 10.53%. Total % P_2O_5 = 10.71.

Thus it may be said that the phosphate present in this fluorspar slag is soluble in 2% citric acid.

The reduction of acidity is greatest in the first treatment and is not directly related to the percentage of soluble "P_2O_5" This reduction of acidity is due to the basic materials, chiefly the calcium compounds, the importance of which has been dealt with by several investigators.

Availability of Calcium present in basic slags.

There is not a standard method for the determination of these compounds.

Hendrick (8) measured the amount of "lime" present in basic

slags capable of acting as a base from the amount of ammonia liberated by distilling together, under standard conditions, samples of basic slag and solutions of ammonium sulphate or chloride, preferably chloride. He concluded that "as the conditions are complex it is impossible to draw any line and state an exact percentage of basic lime in slag except in terms of a strictly defined method of determining it". From the conditions necessary for obtaining concordant results using this method, ease of manipulation is not an outstanding feature.

Vanstone determined the calcium obtained in solution by heating slags of different solubility with ammonium chloride and sulphate solutions. He concluded that "basic slags contain calcium silicates which are readily decomposed" and thus supports the conclusions of Williams (10) that they can supply large amounts of exchangeable calcium. It is suggested that in the soil, after a period of time which will depend on conditions such as organic matter, rainfall and climate, the silicate gives up its lime leaving the phosphate more open to attack. In the case of high soluble slags the period of time may be very short since they have small amounts of calcium silicate but a large amount of easily

soluble phosphate. It is possible that such a slag on very acid soils, applied in relatively small quantity might not supply sufficient exchangeable calcium, whereas a low soluble slag in greater quantity might do so.

Brioux and Jouis (11) determined the neutralising effect by mixing slag and soil. Two grams of slag were mixed dry with one kilo. of soil of known PH: then the moisture content was brought up to 20% and the PH determined by the hydrogen electrode after certain intervals. From the curves, they calculated according to the different PH values the amounts of active lime coming from the fertiliser used. For a soil of rather strong acidity the variations in PH observed 3 hours after mixing corresponds to active lime from 12 - 18%, which is very much higher than the quantity of free lime present. The silicates and silico phosphates existing in basic slag were found to decompose rapidly in an acid solution. They concluded that the amount of active lime in basic slag exceeded 30%.

To obtain a comparison of the basic materials of non fluorspar slag 1 and fluorspar slag 2 available for neutralising soil acidity, varying quantities of the slags were shaken with soil suspensions, (1) in water, (2) in

calcium chloride (.2 Molar) solution. The quantities of materials used were similar to those required for the Hardy and Lewis (12) method of determining "lime requirements" of soils, known weights of slag being used to replace lime water additions.

Experiments were carried out with four soils of different texture classes. PH values after certain periods of shaking were ascertained by the quinhydrone electrode (these may be regarded as 60 sec. values).

The results obtained are given in the following tables.

Table No. 10. Effect of slags on soil PH.

Clay soil - water suspension. (10 gm. soil in 40 cc. water).

Slag No. 1

Wt. of slag.	PH values after shaking period, in hours. (½)	(4)	(24)	(72)	(120)
.00	6.51	6.47	6.43	6.45	6.49
.005	6.68	6.78	6.77	6.72	6.73
.01	6.84	6.92	6.94	7.02	6.96
.02	7.09	7.23	7.36	7.36	7.28
.03	7.32	7.55	7.58	7.56	7.46
.04	7.53	7.71	7.77	7.73	7.49
.05	7.69	7.83	7.84	7.83	7.60

Slag No. 2

	(4)	(24)	(48)	(110)
.00	6.47	6.42	6.43	6.42
.005	6.70	6.72	6.64	6.64
.01	6.86	6.86	6.86	6.84
.02	7.23	7.22	7.23	7.15
.03	7.58	7.58	7.55	7.39
.04	7.83	7.88	7.71	7.48

Table No. 11. Effect of slags on soil PH.

Peaty Soil - water suspension.

Slag No. 1

Wt. of slag.	PH values after shaking period, in hours.				
	(½)	(4)	(24)	(72)	(120)
.00	5.00	4.93	4.91	4.83	4.79
.005	5.07	5.00	5.05	5.02	5.00
.01	5.16	5.16	5.17	5.14	5.11
.02	5.35	5.26	5.38	5.35	5.37
.03	5.54	5.57	5.61	5.59	5.58
.04	5.71	5.78	5.81	5.80	5.83
.05	5.81	5.90	6.02	6.01	6.03
.075	6.11	6.18	6.26	6.25	6.28
.1	6.40	6.52	6.56	6.52	6.58
.125	6.64	6.72	6.80	6.78	6.87
.15	6.86	6.92	7.04	7.09	7.16

Table No. 11 (Contd.)

Slag No. 2

Wt. of Slag.	PH values after shaking period, in hours.			
	(4)	(24)	(48)	(110)
.00	4.95	4.88	4.87	4.78
.005	5.05	4.95	4.95	4.81
.01	5.17	5.09	5.09	4.97
.02	5.35	5.31	5.29	5.26
.03	5.50	5.47	5.45	5.40
.04	5.66	5.65	5.61	5.57
.05	5.76	5.75	5.73	5.73
.075	6.06	6.02	6.01	6.06
.10	6.35	6.35	6.33	6.47
.125	6.56	6.56	6.54	6.72
.15	6.70	6.68	6.73	6.92

Table No. 12 Effect of slags on soil PH.

Medium loam - water suspension.

Slag No. 1

Wt. of Slag.	PH values after shaking period in hours.				
	(½)	(3)	(24)	(48)	(120)
.00	5.07	5.35	5.35	5.29	5.24
.005	5.07	5.40	5.49	5.43	5.40
.01	5.43	5.67	5.71	5.69	5.63
.02	5.67	5.94	6.01	5.97	5.90
.03	5.71	5.99	6.11	6.07	6.06
.04	5.95	6.23	6.35	6.35	6.30
.05	6.11	6.42	6.52	6.54	6.54
.075	6.54	6.72	6.91	6.91	6.96
.1	6.82	6.98	7.15	7.16	7.27
Slag No. 2	(2)	(7)	(24)	(48)	(72)
.00	5.31	5.38	5.38	5.35	5.37
.005		5.52	5.52	5.49	5.52
.01	5.31	5.57	5.56	5.54	5.59
.02	5.87	5.95	5.92	5.88	5.88
.03	5.92	6.09	6.09	6.07	6.04
.04	6.28	6.30	6.30	6.38	6.26
.05		6.40	6.37	6.37	6.37
.075	6.94	6.89	6.89	6.89	6.87
.1	7.16	7.08	7.14	7.14	7.13

Table No. 13. Effect of slags on soil PH.

Light Loam - water suspension.

Slag No. 1

Wt. of slag.	PH value after shaking period, in hours. ($\frac{1}{2}$)	(3)	(24)	(48)	(96)
.00	5.57	5.95	5.97	5.97	5.94
.005	6.04	6.18	6.21	6.16	6.14
.02	6.43	6.58	6.61	6.59	6.59
.04	6.94	6.96	7.02	7.01	6.99
.05	7.08	7.11	7.16		
.075	7.30	7.28	7.34	7.34	7.32
.1	7.49	7.48	7.60	7.64	7.60

Slag No. 2

	(2)	(7)	(24)	(48)	(72)
.00	5.88				5.92
.01	6.07	6.14	6.16	6.12	6.09
.02	6.52	6.49	6.49	6.43	6.40
.05	7.02	6.96	6.96	6.94	6.91
.075	7.49	7.39	7.37	7.34	7.28
.10	7.75	7.67	7.67	7.66	7.56

Summary of Results.

The results show that with reference to neutralisation of soil acidity as manifest in the water suspensions prepared, of the four soils of different texture classes, the slags are approximately of equal value: and that the period of shaking, within the limits given, does not appreciably affect the result.

Table No. 14. Effect of slags on soil PH.

Clay soil - (.2 M Calcium Chloride suspension.

10 gm. soil in 40 cc. .. .. $CaCl_2$.

Slag No. 1

Wt. of slag.	PH value after shaking period in hours. (36)	(108)	>108
.00	5.49	5.47	
.005	5.78	5.76	
.02	6.28	6.14	6.20
.03	6.51	6.43	
.04	6.67	6.59	6.68
.05	6.75	6.75	
.06			6.92
.08			7.18

Slag No. 2	(27)	>108
.00	5.5	
.02	6.26	6.37
.04	6.86	6.94
.05	7.11	7.18
.06		7.42
.08		7.75

Table No. 15. Effect of slags on soil PH.

Peaty soil - Calcium Chloride Suspension.

Slag No. 1

Wt. of slag.	PH value after shaking period in hours. (36)	(108)
.00	4.05	3.97
.02	4.41	4.38
.04	4.77	4.77
.06	5.14	5.14
.08	5.35	5.35
.10	5.50	5.54
.12	5.59	5.61
.14	5.75	5.78
.16	5.95	5.95
.40		6.8

Table No. 15 (Contd.)

Slag No. 2

Wt. of slag.	PH value after shaking period in hours. (26)
.00	4.07
.05	4.77
.10	5.28
.15	5.59
.175	5.76
.20	5.99
.225	6.12
.25	6.32
.30	6.54
.40	7.23

Table No. 16. Effect of slags on soil PH.

Medium Loam - Calcium Chloride Suspension.

Slag No. 1

Wt. of slag.	PH values after shaking period, in hours.		
	(22)	(52)	(124)
.00	4.41	4.41	4.36
.01	4.66	4.57	4.70
.03	5.05	5.05	5.14
.05	5.40	5.50	5.50
.10	5.94	6.14	6.23
.20		6.70	
.22		6.75	
.24		6.82	

Slag No. 2

	(26)
.00	4.46
.03	4.98
.07	5.54
.10	5.95
.20	6.70
.22	6.91
.24	7.01

Table No. 17. Effect of slags on soil PH.

Light Loam - Calcium Chloride Suspension.

Slag No. 1

Wt. of slag.	PH values after shaking period, in hours. (22)	(52)	(124)
.00	4.90	4.85	4.91
.06	6.20	6.16	6.20
.08	6.20	6.40	6.43
.10	6.43	6.63	6.68
.12		6.80	
.14		6.90	
.16		6.99	

Slag No. 2	(26)	(124)
.00	4.91	
.06	6.06	6.21
.10	6.56	
.14	6.94	7.06
.16	7.08	7.28
.18	7.28	

Summary of Results.

With the calcium chloride suspensions, giving calcium saturation of the soil and decreased initial PH value, the fluorspar slag shows an advantage over the non-fluorspar slag in bringing the suspension to the neutral point PH 7, under the conditions of the test. Increased amounts of slags over these required for water suspensions are required to give neutrality. With prolonged shaking increase of PH is noted in some cases.

EXAMINATION OF FLUORSPAR BALL SLAGS.

Introductory.

Sullwald (13) in a study of Thomas slags found that when these were cooled in large blocks the total and citric acid soluble phosphoric acid increased regularly from the outside to the middle.

So far as the Author is aware, no such examination of fluorspar slags has been previously made. The following is a study of this matter on two slags of different origin.

Cargo Fleet Ball Slag.

Samples were taken (A) from the outside of the slag ball, (B) from midway between the outside and the centre, (C) from the centre of the ball.

The chemical composition of these samples has been determined in portions ground as for fertiliser use. Solubility, in 2% citric acid solution, of the phosphate, calcium, and silica present has also been ascertained.

Fineness of ground samples.

The fineness was determined, as in previous experiments, by sieving into five fractions.

Table No. 18. Fineness of Cargo Fleet Ball Slags.

Fraction	(A)	(B)	(C)
1	17.6	18.8	18.9
2	15.1	13.9	14.6
3	11.1	10.1	11.6
4	21.3	28.4	29.3
5	34.7	28.6	25.5

Table No. 19. Chemical Composition of Cargo Fleet Ball Slags.

	(A)	(B)	(C)
% CaO	47.70	47.00	47.10
% P_2O_5	13.70	13.58	13.82
% SiO_2	18.60	19.00	19.00
% MgO	3.76	3.63	3.72
% Al_2O_3	3.97	3.81	3.88
% FeO	4.58	4.70	3.92
% Fe_2O_3	1.72	1.50	2.31
% MnO	3.31	3.38	3.42
% S	.66	.71	.85

Table No. 20. Molecular concentrations of Cargo Fleet BallSlags

	(A)	(B)	(C)
CaO	.851	.838	.840
P_2O_5	.0964	.0956	.0972
SiO_2	.308	.315	.315
MgO	.093	.090	.090
Al_2O_3	.0389	.0373	.0380
FeO	.0638	.0654	.0546
Fe_2O_3	.0108	.0094	.0145
MnO	.0467	.0477	.0482

Molecular formulae.

(A)

CaO	.851	Fe_2O_3	.0108	SiO_2	.308
MgO	.093	Al_2O_3	.0389	P_2O_5	.0964
MnO	.0467				
FeO	.0638				

i.e. RO : .046 R_2O_3 : .292 SiO_2, .0914 P_2O_5

(B)

CaO	.838	Fe_2O_3	.0094	SiO_2	.315
MgO	.090	P_2O_5	.0373	P_2O_5	.0956
MnO	.0477				
FeO	.0654				

i.e. RO : .045 R_2O_3 : SiO_2 .303, P_2O_5 .092

(C)

CaO	.840	Fe_2O_3	.0145	SiO_2	.315
MgO	.092	Al_2O_3	.0380	P_2O_5	.0972
MnO	.0482				
FeO	.0546				

i.e. RO : .0507 R_2O_3 : SiO_2 .304, P_2O_5 .0939

Table No. 21. Citric Acid Solubility Sample A.

(5 gm. slag in 500 cc. 2% Citric acid solution shaken at 30 rev/min.)

Period of shaking (in hours)	Acidity of extract.	% Soluble CaO	% Soluble P_2O_5	% Soluble SiO_2
½	50 cc= 8.15 ccN	26.92	1.06	15.26
1	" 7.64 "	27.74	1.10	15.67
2	" 7.28 "	27.95	1.11	15.59
> 2	" 6.62 "	28.00	1.146	13.93
> 12	" 6.32 "	28.40		14.39
Repeated ½ hour extractions (.8 gm. slag in 80 cc.2% citric acid)				
Extract No. 1		26.4	1.09	14.74
" 2		3.67	1.29	.80
" 3		2.78	1.40	.12
" 4		2.95	1.75	
" 5			1.73	
Repeated 1 hour extractions.				
Extract No. 1	50 cc= 7.79 cc N.	28.21	1.23	14.64
" 2	" 12.84 "	3.94	1.75	
" 3	" 13.4 "		2.03	
" 4	" 13.6 "		1.91	

Table No. 22. Citric Solubility Sample B.

(5 gm. slag in 500 cc. 2% citric acid solution shaken at 30 rev/min.)

Period of shaking (in hours)	Acidity of extract	% Soluble CaO	% Soluble P_2O_5	% Soluble SiO_2
½	50 cc=8.15 cc N	27.28	1.23	
1	" 7.64 "	27.49	1.22	15.37
2	" 7.28 "	27.90	1.23	15.29
> 2	" 6.78 "	26.92	1.05	13.68
> 12	" 6.32 "	28.50	1.06	15.34
Repeated ½ hour extractions.				
Extract No. 1		26.78	1.19	15.12
" 2		3.69	1.35	.82
" 3		2.83	1.47	.12
" 4		3.1	1.55	
" 5			1.67	
Repeated hour extractions.				
Extract No. 1	50 cc ≡ 7.71 cc N	28.06	1.33	14.33
" 2	" 12.84 "	4.10	1.91	
" 3	" 13.4 "		2.125	
" 4	" 13.6 "		1.98	

Table No. 23. Citric Solubility Sample C.

(5 gm. slag in 500 cc. 2% citric acid solution shaken at 30 rev/min.)

Period of shaking (in hours)	Acidity of extract	% Soluble CaO	% Soluble P_2O_5	% Soluble SiO_2
½	50 cc ≡ 8.0 cc N	29.8	2.72	15.49
1	" 7.69 "	30.1	2.60	15.03
2	" 7.33 "	30.53	2.59	
> 2	" 6.58 "	29.72	2.53	14.09
>12	" 6.25 "	30.92	2.53	15.27
Repeated ½ hour extractions.				
Extract No. 1		30.1	2.48	14.90
" 2		3.89	1.82	.34
" 3		3.15	1.75	.22
" 4		2.49	1.38	
" 5		2.00	.75	
Repeated hour extractions.				
Extract No. 1	50 cc ≡ 7.64 cc N	32.24	2.49	15.51
" 2	" 12.84 "	4.43	2.33	
" 3	" 13.4 "	3.61	2.22	
" 4	" 13.6 "		1.50	

Table No. 24. Molecula

Ordinary Method

Period of shaking (in hours)	CaO
½	.480
1	.495
2	.498
> 2	.499
>12	.506

Repeated ½ hour extracti

Extract 1	.470
" 2	.0655
" 3	.050
" 4	.0526
" 5	

Repeated hour extraction

Extract 1	.503
" 2	.0703
" 3	
" 4	

Table No. 24. Molecular Ratios of soluble constituents.

Ordinary Method

Period of shaking (in hours)	Sample A			Sample B			Sample C		
	CaO	P_2O_5	SiO_2	CaO	P_2O_5	SiO_2	CaO	P_2O_5	SiO_2
½	.480	.00746	.253	.487	.00865		.531	.0192	.257
1	.495	.00741	.260	.490	.00858	.255	.537	.0183	.249
2	.498	.00781	.258	.498	.00865	.253	.544	.0182	
> 2	.499	.00806	.231	.480	.00739	.227	.530	.0178	.234
>12	.506		.238	.508	.00746	.254	.552	.0178	.253
Repeated ½ hour extractions.									
Extract 1	.470	.00767	.244	.477	.00837	.251	.537	.0175	.247
" 2	.0655	.00929	.0133	.0658	.0095	.0136	.0694	.0128	.0056
" 3	.050	.00985	.0020	.0505	.0103	.002	.0562	.0123	.0036
" 4	.0526	.0123	.00166	.0553	.0109		.0444	.0097	
" 5		.0118			.0117		.0357	.0053	
Repeated hour extractions.									
Extract 1	.503	.0086	.243	.500	.0094	.238	.575	.0175	.257
" 2	.0703	.0123		.0731	.0134		.079	.0164	
" 3		.0143			.0149		.0644	.0156	
" 4		.0134			.0139			.0105	

Discussion of Results.

Slight differences only in the chemical composition of the samples from the outside, midway, and centre, occur. Examination of the molecular formulae shows that there is not sufficient calcium present to combine with the silica and with the phosphoric oxide to give dicalcium silicate and apatite respectively: so that probably some of the magnesium takes the place of calcium in the silicate. Citric acid solubility with reference to soluble phosphate is typical of fluorspar slags. No increase in % soluble P_2O_5 is obtained by increasing the time of shaking. In some cases a decrease results. The sample from the centre of the ball shows greatest amount of soluble P_2O_5; that from the outside of the ball lowest, where one treatment with citric acid is given. This is probably due to differences in physical states of the samples since no explanation is to be obtained from fineness and chemical composition figures.

The large amounts of "CaO" and "SiO_2" in contrast with the small amounts of "P_2O_5" that are soluble in 2% citric acid on initial treatment demonstrate that these are not combined together to form one compound.

On repeated treatment most of the calcium and silica is soluble and found to be present in the first extract, and

consequently a greater reduction in the acidity of the original acid solution is noted. In some cases the % soluble P_2O_5 figure obtained by shaking the residue with an equal quantity of 2% citric acid solution exceeds that for the first extraction. This may be due to the increased ratio of citric acid to solid material and also to the fact that since most of the calcium has been dissolved reduction of the acidity of the solvent is not so great, and the solvent is consequently more active.

Acklam Ball Slag.

Samples were obtained as in the case of the Cargo Fleet Slag. Thin sections were prepared from the "lump" samples and examined microscopically, especially for the nature of the phosphate present, since these slags had been produced under ordinary working conditions soon after the claim had been made that less fluorspar was being used in the basic open hearth process, with a favourable effect on the citric acid solubility. The chemical composition fineness and citric acid solubility of samples ground as for fertiliser use were also determined.

Table No. 25. Fineness of Acklam Ball Slags.

Fraction	(A)	(B)	(C)
1	18.4	12.6	8.8
2	14.1	6.3	8.6
3	7.0	8.2	8.5
4	25.0	31.8	37.8
5	35.5	41.1	36.3

Table No. 26. Chemical composition of Acklam Ball Slags.

Sample	(A)	(B)	(C)
% CaO	46.01	44.56	45.75
% P_2O_5	17.54	19.60	18.04
% SiO_2	15.00	14.40	14.00
% MgO	6.62	6.46	6.01
% Al_2O_3	4.24	4.33	4.14
% FeO	6.80	4.50	5.70
% Fe_2O_3	2.41	1.65	2.60
% MnO	1.21	1.24	2.08
% S	1.25	1.16	1.46

Table No. 27. Molecular concentrations.

	(A)	(B)	(C)
CaO	.821	.795	.816
P_2O_5	.123	.138	.127
SiO_2	.249	.239	.232
MgO	.164	.160	.149
Al_2O_3	.0415	.0424	.0405
FeO	.0947	.0627	.0794
Fe_2O_3	.0151	.0103	.0163
MnO	.0171	.0175	.0293

Molecular formulae of Acklam Ball Slag Samples.

(A)

CaO	.821				
MgO	.164	Fe_2O_3	.0151	SiO_2	.249
MnO	.0171	Al_2O_3	.0415	P_2O_5	.123
FeO	.0947				

i.e. RO : .0516 R_2O_3 : .227 SiO_2 / .113 P_2O_5

(B)

CaO	.795				
MgO	.160	Fe_2O_3	.0103	SiO_2	.239
MnO	.0175	Al_2O_3	.0424	P_2O_5	.138
FeO	.0627				

i.e. RO : .0509 R_2O_3 : SiO_2 .231 / P_2O_5 .133

(C)

CaO	.816				
MgO	.149	Fe_2O_3	.0163	SiO_2	.232
MnO	.0293	Al_2O_3	.0405	P_2O_5	.127
FeO	.0794				

i.e. RO : .0529 R_2O_3 : SiO_2 .216 / P_2O_5 .118

Consideration of above shows that there is insufficient "CaO" to give all the "P_2O_5" as apatite and "SiO_2" as dicalcium silicate, so that as with Cargo Fleet Ball Slags, and as found by Scott and McArthur (1), MgO is probably replacing "CaO" in the silicate.

Table No. 28. Citric Solubility of Acklam Ball Slag, Sample A from the outside of ball.

(5 gm. slag in 500 cc. 2% citric acid solution, shaken at 30 rev/min.)

Period of shaking (in hours)	Acidity of extract	% Soluble CaO	% Soluble P_2O_5	% Soluble SiO_2
2		20.74	2.69	11.5
24		21.20	2.75	12.34

Repeated hour extractions.

Extract No. 1	50 cc ≡ 9.3 cc N	19.05	2.34	
2	" 12.85 "	8.31	3.36	
3	" 13.55 "	6.97	3.60	
4	" 13.7 "	6.05	3.05	
5	" 13.85 "		2.17	

Molecular Ratios of above.

Sol. CaO	Sol. P_2O_5	Sol. SiO_2
.370	.019	.191
.378	.019	.204
.34	.0165	
.148	.0236	
.124	.0253	
.108	.0215	
	.0153	

Table No. 29. Citric solubility of Acklam Ball Slag, Sample B

Midway to centre.

(5 gm. in 500 cc. 2% citric acid solution shaken at 30 rev/min)

Period of shaking (in hours)	Acidity of extract	% Soluble CaO	% Soluble P_2O_5	% Soluble SiO_2
2		20.45	2.5	11.00
24		20.81	2.64	11.35

Repeated hour extractions.

Extract No. 1	50 cc ≡ 9.4 cc N	19.50	2.62	
2	" 13.1 "	7.52	3.35	
3	" 13.5 "	5.80	3.075	
4	" 13.8 "	4.53	2.036	
5	" 13.85 "		1.68	

Molecular ratios of above.

Sol. CaO	Sol. P_2O_5	Sol. SiO_2
.365	.0176	.182
.371	.0185	.188
.348	.0184	
.134	.0236	
.1035	.0216	
.0818	.0143	
	.0118	

Table No. 30. Citric solubility of Acklam Ball Slag, Sample C Centre of Ball.

(5 gm. in 500 cc. 2% citric acid solution, shaken at 30 rev/min

Period of shaking (in hours)	Acidity of extract	% Soluble CaO	% Soluble P_2O_5	% Soluble SiO_2
2		23.74	3.43	11.35
24		23.75	3.69	11.61

Repeated hour extractions.

Extract No. 1	50 cc ≡	8.95	ccN	23.55	3.31
2	"	13.05	"	4.90	3.47
3	"	13.60	"	4.23	3.20
4	"	13.90	"	3.73	1.97
5	"	13.95	"	2.19	1.23

Molecular ratios of above.

Sol. CaO	Sol. P_2O_5	Sol. SiO_2
.423	.0241	.188
.423	.0260	.192
.420	.0233	
.0874	.0244	
.0754	.0225	
.0664	.0139	
.0391	.0087	

Summary of results.

The results obtained show, as with Cargo Fleet Ball Slags, no outstanding differences in chemical composition of the samples taken from different parts of the "ball". It is noteworthy that % FeO is highest in the sample from the outside of the ball.

The greater solvent power of citric acid for calcium, as compared with phosphorus, in these samples of fluorspar slag is again demonstrated. The reduction of acidity with increase in % soluble CaO is well marked.

In each case the % soluble P_2O_5 obtained from treatment of the residue with 2% citric acid exceeds that of the first extraction.

The percentage solubility of the "P_2O_5" with one treatment is greatest in sample from the centre of the ball. The results obtained indicate that with sufficient repetition of of treatment all the phosphate present is soluble in citric acid.

Microscopic Examination of Acklam Ball Slag.

This consisted of examination of thin slides of the various samples, in transmitted light.

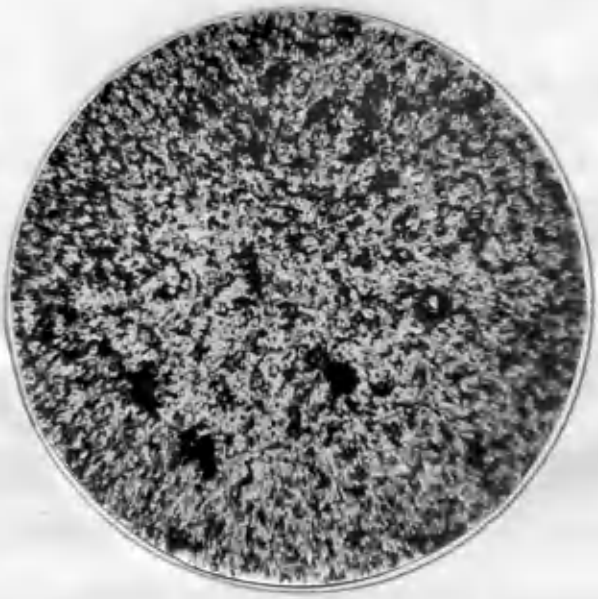
Sample (A). This specimen was a fine grained aggregate

of colourless transparent crystals, occasionally occurring as small laths, and dark coloured material, translucent or opaque, present in characteristic rounded form.

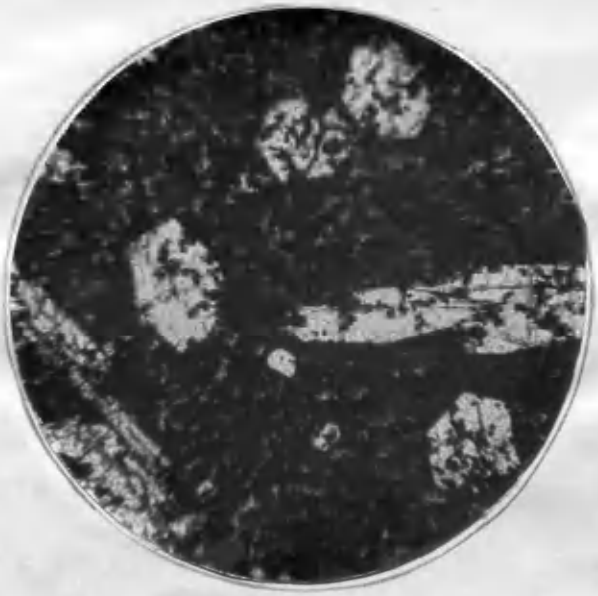
At high magnification, the transparent material was found to be composed of two different materials (1) Laths with high refractive index, low double refraction, and showing straight extinction - optical properties of apatite, (2) Irregular crystals, in some cases slightly stained, with high refractive index and low double refraction. The double refraction was however higher than that of the preceding type. The properties agree with the optical props. of dicalcium silicate.

Sample (B). The thin section of this sample showed the presence of relatively abundant colourless crystals with well defined crystal faces. These crystals were of a large size and of a porphyritic nature. In cross-section they were hexagonal, and often contained inclusions. The optical properties agreed exactly with those of apatite - high refractive index, low double refraction, straight extinction.

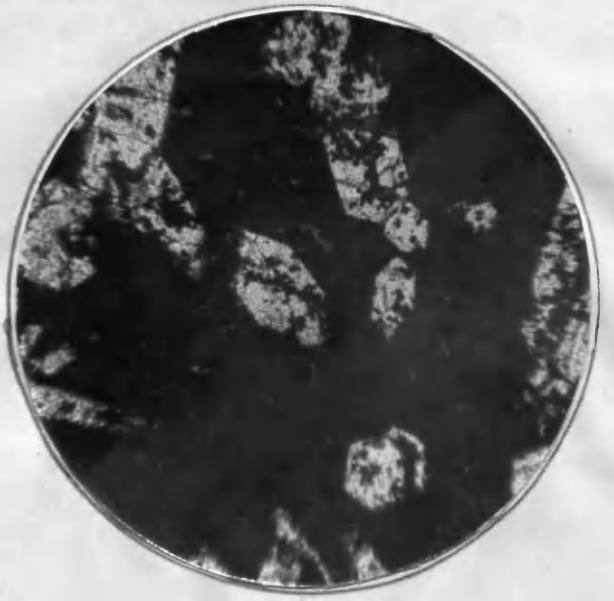
The section also showed a large number of smaller irregular crystals, which had a "frosted" appearance, probably indicating alteration. The properties were in agreement with those of dicalcium silicate.



A.



B



C.

Very small amounts of colourless material of high double refraction were also noted. This occurred between crystals of apatite and the silicate.

The matrix as in (A) was composed of rounded translucent or opaque grains. In this section, they were larger.

Sample (C). This section was similar to that of sample (B). The differences in texture and crystal size are shown in the photographs opposite. Those of (B) and (C) were taken to show primarily the nature of the apatite crystals, in reality the ground mass is not so dark as it appears in the photographs.

Solubility of Basic Slags in Standard Acid Solutions.

The citric acid solubility figures obtained in the preceding work have shown that, with fluorspar slags, two per cent. citric acid solution is a better solvent for the calcium present than for the phosphorus, the reaction with the calcium compounds reducing the acidity of the solution. This probably affects the solubility of the phosphorus compounds, and is further evidence of the empirical nature of the citric acid test in dealing with slags showing variations in calcium content.

To determine the effect of acidity on the solubility of the calcium, silicon, and phosphorus contained in (1) Non-fluorspar slag (Nov. 1930) No. 1.

(2) Fluorspar slag (Nov. 1930) No. 2.

(3) Acklam Ball Slag - Sample A from the outside of the "ball"

(4) " " " C " " centre " "

a series of tests were carried out using buffered acid solutions of known PH value and standard acidity.

The standard solutions were mixtures of sodium acetate and hydrochloric acid, made up according to figures published by Britton (14).

The method employed was similar to that of official method for the citric acid test - 5 gm. samples of the slags,

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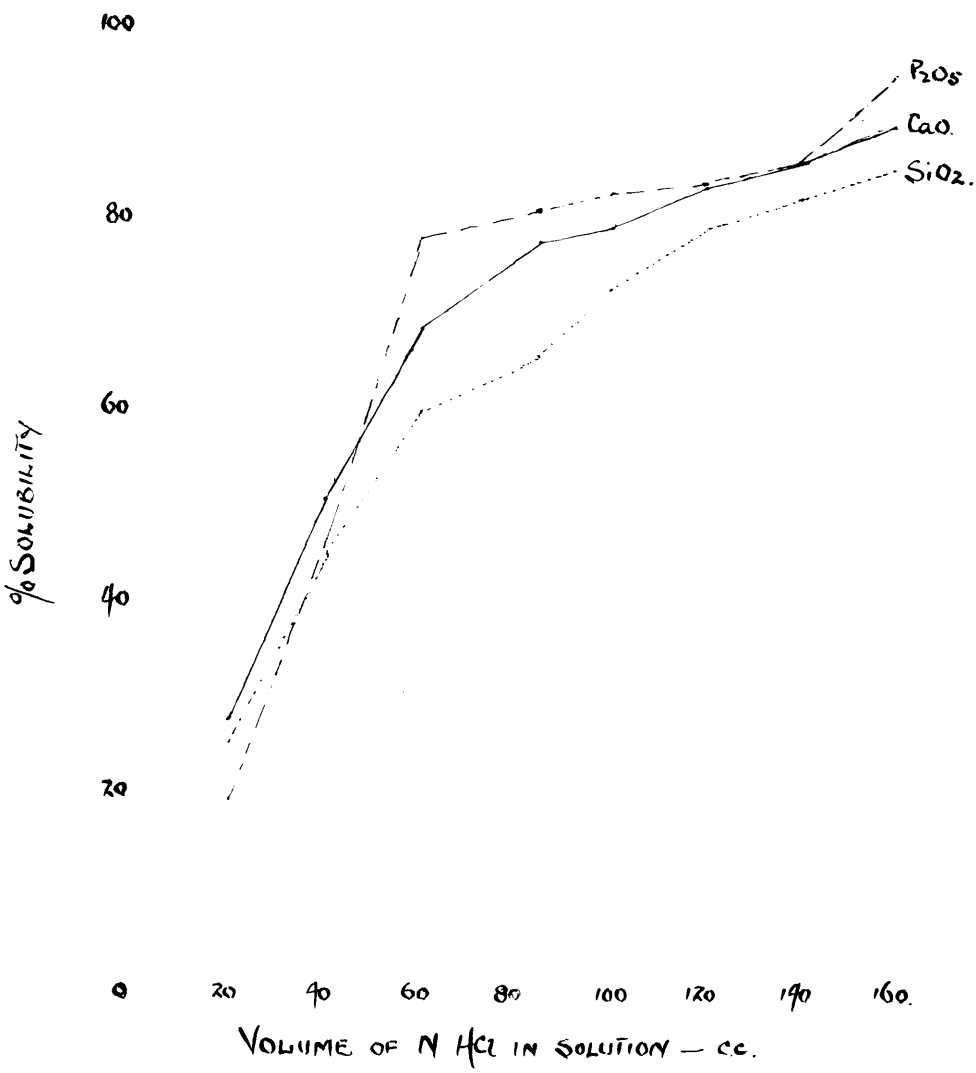
GRAPHS SHOWING RELATION BETWEEN PERCENTAGE SOLUBILITY AND INITIAL ACIDITY OF SOLUTION — NON-FLUORSPAR SLAG No. 1.



of fineness already noted, shaken at room temperature for 1 hour at 30 revs/min. At the end of the shaking period the residue was separated from the solution by filtration, the extract being immediately analysed.

PH values were determined by the quinhydrone electrode - 60 second values.

Table No. 31. Solubility of non-fluor. slag No.1 in standard acid solutions.

Solution No.	1	2	3	4	5	6	7	8
Volume of N Hcl in 500 cc.	160	140	120	100	85	60	40	20
Volume of N.Sodium acetate in 500 cc	100	100	100	100	100	100	100	100
pH (Theor)	.91	1.09	1.42	2.64	3.79	4.39	4.76	5.2
pH (Determined)	.90	1.10	1.43	2.66	3.81	4.39	4.78	5.23
Extract PH -	3.3	3.82	4.13	4.46	4.72	5.20	5.67	6.40
Colour	blue	bluish	yellow	yellow	yellow	yellowish	colourless	
Acidity of 500cc=	106.2 ccN	92.2 ccN	76.4 ccN	60 ccN	46.2 ccN	24.8 ccN	11.1 ccN	1.83 ccN
Reduction of acidity cc.N	53.8	47.8	43.6	40.0	38.8	35.2	28.9	18.2
% Soluble CaO	39.2	37.45	36.4	34.8	33.9	29.9	22.07	12.03
% Soluble P_2O_5	11.82	10.7	10.43	10.28	10.05	9.71	5.77	2.5
% Soluble SiO_2	9.28	8.97	8.64	7.92	7.16	6.54	4.85	2.70
% Solubility CaO	89.1	85.13	82.73	78.38	77.05	67.97	50.16	27.34
% Solubility P_2O_5	94.2	85.2	83.1	81.9	80.07	77.38	45.98	18.77
% Solubility SiO_2	84.35	81.55	78.54	71.99	65.09	59.46	44.09	24.55
Molecular Ratios.								
Soluble CaO	8.40	8.86	8.87	8.58	8.55	7.82	9.69	12.2
Soluble P_2O_5	1	1	1	1	1	1	1	1
Soluble SiO_2	1.85	1.97	1.96	1.82	1.68	1.59	1.98	2.55

GRAPHS SHOWING RELATION BETWEEN PERCENTAGE SOLUBILITY AND INITIAL ACIDITY OF SOLUTION — FLUORSPAR SLAG, NO. 2..

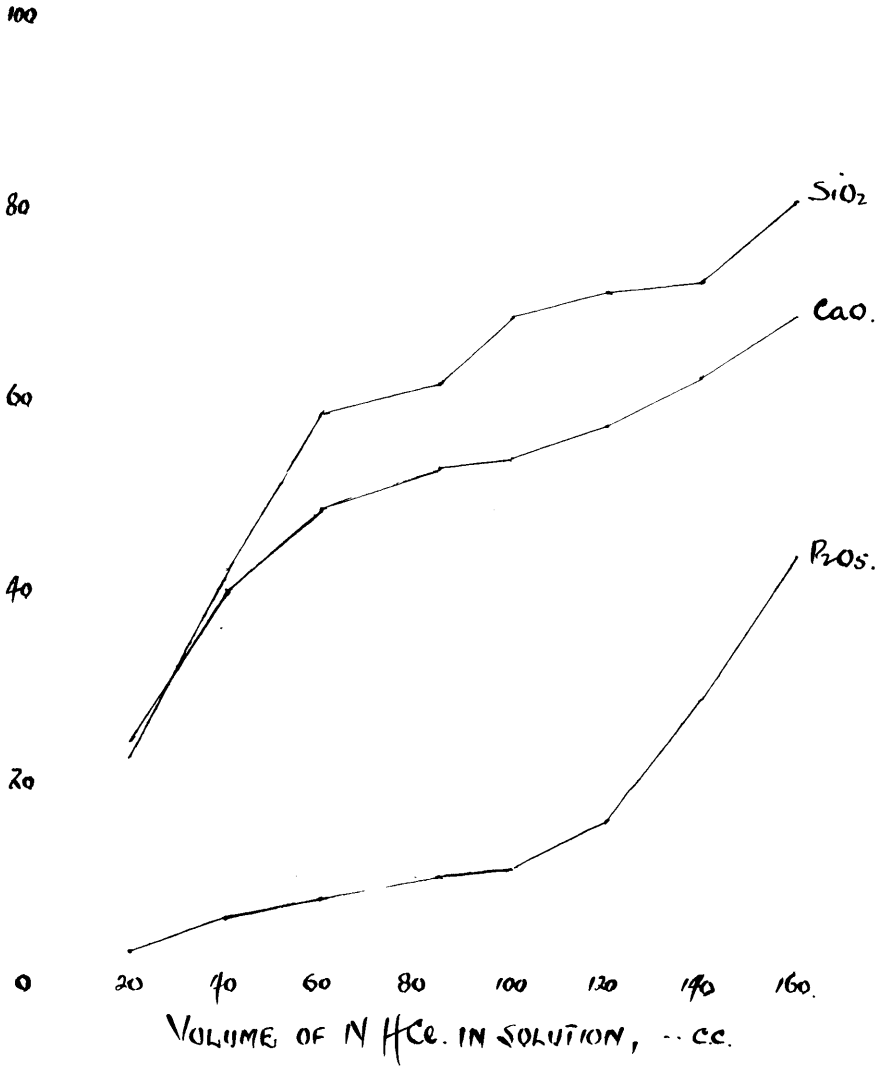


Table No. 32. Solubility of Fluorspar Slag No. 2 in standard acid solutions.

Solution No.	1	2	3	4	5	6	7	8
	Composition as in solutions for Slag No. 1.							
Extract								
PH	3.51	4.10	4.50	4.85	4.97	5.09	6.18	7.66
Colour.			Colourless					
Acidity of 500 cc in cc.N	95.8	80.4	66.0	46.15	34.75	13.40	3.69	.25alk
Redn. of Acidity in cc.N	64.2	59.6	54.5	53.85	50.25	46.6	37.3	20.25
% Sol.CaO	33.6	30.45	28.05	26.4	25.9	23.8	19.48	11.87
% Sol.P_2O_5	4.63	3.03	1.69	1.15	1.05	.836	.59	.231
% Sol.SiO_2	11.51	10.30	10.15	9.74	8.78	8.35	6.02	3.23
% Solubility CaO	68.3	61.9	57.1	53.7	52.7	48.4	39.6	24.1
% Solubility P_2O_5	43.25	28.3	15.8	10.75	9.8	7.81	5.51	2.15
% Solubility SiO_2	80.5	72.0	71.0	68.2	61.4	58.4	42.1	22.6
Molecular Ratios	**CaO : P_2O_5 : SiO_2**							
Soluble CaO	18.4	25.5	42.1	58.2	62.5	72.2	83.5	130.5
Soluble P_2O_5	1	1	1	1	1	1	1	1
Soluble SiO_2	5.86	8.02	14.15	19.95	19.7	23.55	24.03	33.05

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GRAPHS SHOWING RELATION BETWEEN PERCENTAGE SOLUBILITY AND INITIAL ACIDITY OF SOLUTION. — ACKLAM BALL SLAG - SAMPLE (A)

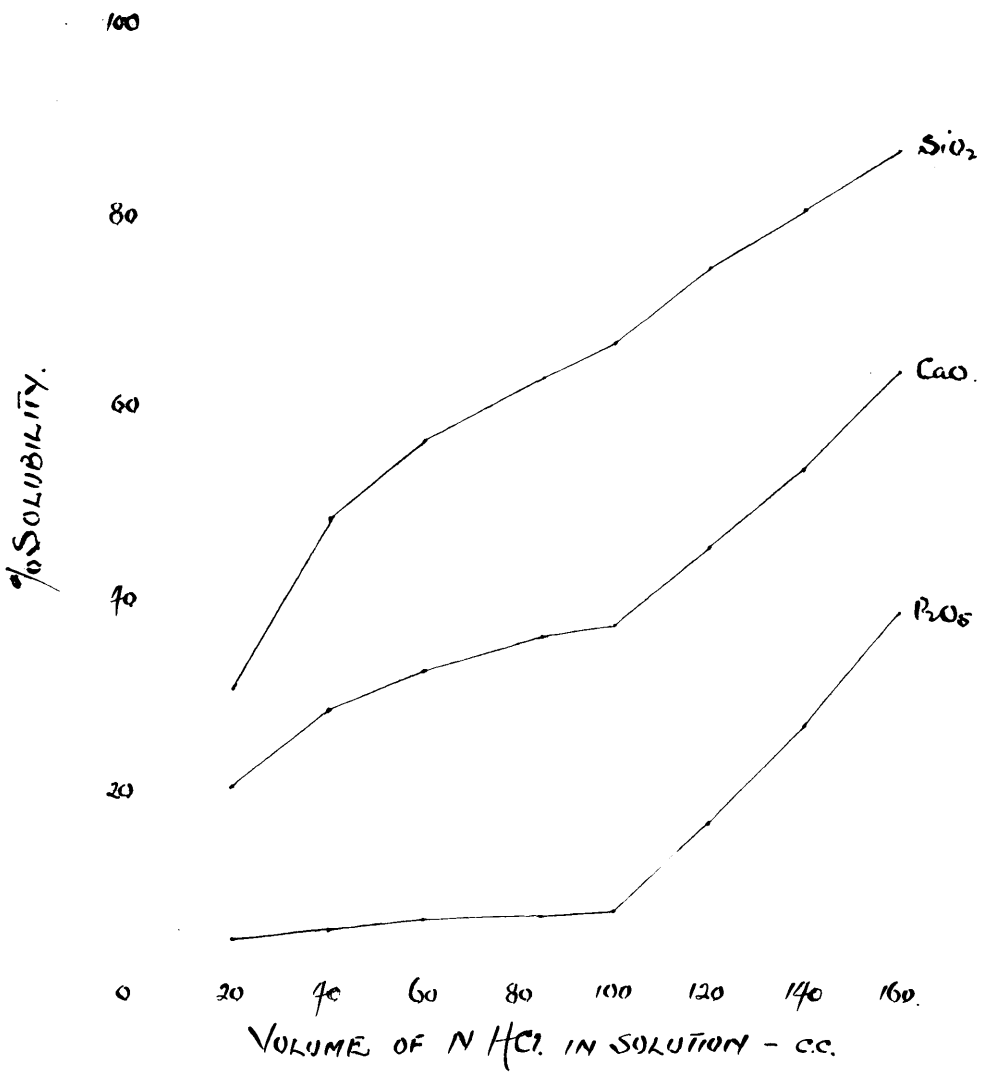

Table No. 33. Solubility of Acklam Ball Slag - Sample A, from the outside of the "ball" in standard acid solutions.

Solution No.	1	2	3	4	5	6	7	8
	Composition as in solutions for No.1 Slag							
Extract								
PH	3.42	3.88	4.24	4.48	4.72	4.98	6.02	6.47
Colour	Colourless							
Acidity of 500 cc in cc.N	99.26	87.35	73.96	58.57	46.16	24.82	10.25	1.5
Reduction of acidity in cc.N	60.74	52.65	46.04	41.43	38.84	35.18	29.75	18.5
% Soluble CaO	29.2	24.55	20.86	16.95	16.52	14.84	13.03	9.36
% Soluble P_2O_5	6.71	4.63	2.89	1.295	1.16	1.114	.926	.75
% Soluble SiO_2	12.97	12.09	11.13	9.98	9.46	8.46	7.24	4.55
% Solubility CaO	63.5	53.4	45.3	36.9	35.9	32.3	28.3	20.3
% Solubility P_2O_5	38.25	26.4	16.5	7.38	6.62	6.35	5.28	4.28
% Solubility SiO_2	86.48	80.58	74.18	66.53	63.06	56.4	48.26	30.33
Molecular Ratios.								
Soluble CaO	11.01	13.44	18.29	33.16	36.08	33.77	35.66	31.61
Soluble P_2O_5	1	1	1	1	1	1	1	1
Soluble SiO_2	4.55	6.15	9.08	18.16	19.22	17.89	18.41	14.3

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GRAPHS SHOWING RELATION BETWEEN.
PERCENTAGE SOLUBILITY AND INITIAL ACIDITY
OF SOLUTION — HEKLAM BALL SLAG - SAMPLE-(C).

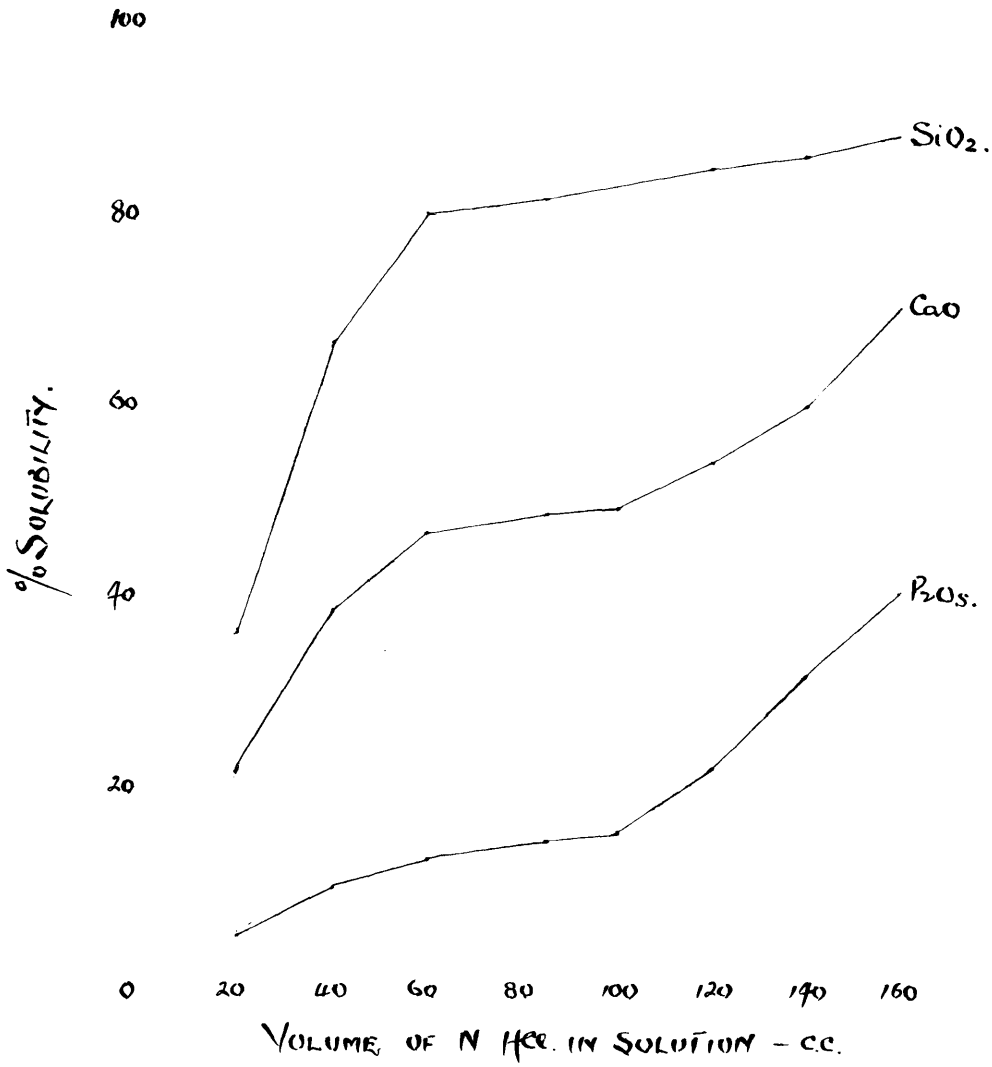


Table No. 34. Solubility of Acklam Ball Slag - Sample C, from centre of "ball" in standard acid solutions.

Solution No.	1	2	3	4	5	6	7	8
	Composition as in solutions for No. 1.							
Extract								
PH	3.93	4.37	4.70	4.81	5.13	5.59	6.06	7.23
Colour	Colourless							
Acidity of 500 cc.in cc.N	99.51	82.88	70.98	52.61	39.22	14.4	4.26	0.0
Reduction of acidity in cc.N	60.49	57.12	49.02	47.39	45.78	45.6	35.74	20
% Soluble CaO	31.83	27.16	24.55	22.31	22.12	21.28	17.65	9.85
% Soluble P_2O_5	7.20	5.63	3.93	2.71	2.54	2.25	1.72	.79
% Soluble SiO_2	12.00	11.97	11.8		11.36	11.15	9.28	5.04
% Solubility CaO	69.6	59.4	53.7	48.8	48.4	46.5	38.6	21.5
% Solubility P_2O_5	39.9	31.2	21.8	15.03	14.1	12.5	9.54	4.38
% Solubility SiO_2	87.7	85.5	84.3		81.2	79.6	66.3	36.0
Molecular Ratios.								
Soluble CaO	11.19	12.23	15.83	20.85	22.1	23.95	26.00	31.59
Soluble P_2O_5	1	1	1	1	1	1	1	1
Soluble SiO_2	3.93	5.01	7.07		10.55	11.67	12.71	15.03

Discussion of results.

Reduction of acidity. This value in every case decreases with decreasing quantity of hydrochloric acid present in the original solution. Comparison of the figures obtained with the different slags shows that the reduction of acidity is least with the non-fluorspar slag, although the actual amount of calcium oxide in solution exceeds that obtained with the fluorspar slags. The values, tabulated below, in terms of volume in cubic centimetres of normal solution, are due to reaction with 5 grams of the slag samples.

Table No. 35. Reduction of acidity.

Solution	Slag No. 1	Slag No. 2	Acklam Ball Slag.	
			Sample A	Sample C
1	53.8	64.2	60.74	60.49
2	47.8	59.6	52.65	57.12
3	43.6	54.5	46.04	49.02
4	40.0	53.85	44.43	47.39
5	38.8	50.25	38.84	45.78
6	35.2	46.6	35.18	45.6
7	28.9	37.3	29.75	35.74
8	18.2	20.25	18.5	20

Table No. 36. Soluble CaO in grams from 5 gm. of slag.

	Slag No.1	Slag No.2	Acklam Ball Slag. Sample A	Sample C
Total CaO in 5 gm. sample	2.2 gm.	2.46 gm.	2.3 gm.	2.29 gm.
Extract				
1	1.96	1.68	1.46	1.59
2	1.87	1.52	1.23	1.36
3	1.82	1.40	1.43	1.23
4	1.74	1.32	0.85	1.12
5	1.69	1.29	0.826	1.11
6	1.50	1.19	.742	1.06
7	1.10	.974	.652	.883
8	.602	.594	.468	.493

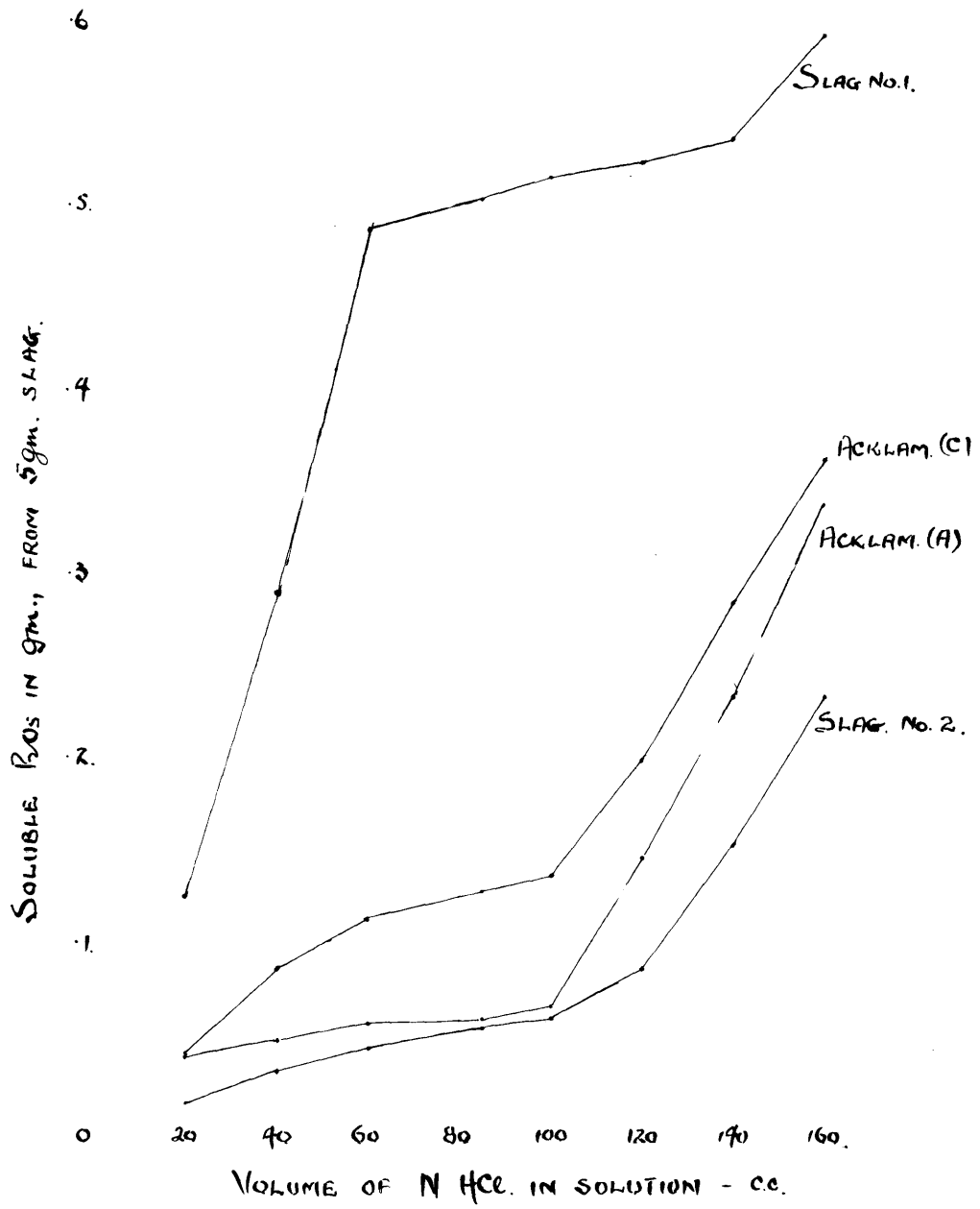
Soluble Phosphoric oxide.

With all four slags the more strongly acid the extracting solution the more phosphoric oxide is found present in solution

Table No. 37. Soluble "P_2O_5" in grams from 5 gm. of slag.

Extract	Slag No.1	Slag No.2	Acklam A	Acklam C
1	.591	.232	.336	.360
2	.535	.151	.232	.282
3	.522	.085	.145	.197
4	.514	.0575	.0648	.136
5	.503	.0525	.058	.127
6	.486	.0418	.0552	.113
7	.289	.0295	.0463	.086
8	.125	.0116	.0375	.0395
Total P_2O_5 present	.628	.536	.877	.902

GRAPHS SHOWING RELATION BETWEEN AMOUNT OF SOLUBLE P_2O_5 AND INITIAL ACIDITY OF SOLUTIONS.



These values are plotted against the volume of Normal hydrochloric acid contained in 500 cc. of original solutions, in graphs on the page opposite.

The graphs demonstrate the difference in the nature of the phosphate contained in the non-fluorspar and the fluorspar slags.

Soluble Silica. The figures for soluble silica are similar to those for soluble "CaO" and "P_2O_5" in the respect that diminishing amounts are found in solution with decrease in acidity.

Table No. 38. Soluble "SiO_2" in gm. from 5 gm. of slag.

Extract	Slag No. 1	Slag No. 2	Acklam A	Acklam C
1	.464	.576	.649	.60
2	.449	.515	.605	.599
3	.432	.507	.557	.59
4	.396	.487	.499	
5	.358	.439	.473	.568
6	.327	.418	.423	.558
7	.243	.308	.362	.464
8	.135	.162	.228	.252

Molecular ratios of soluble CaO : P_2O_5 : SiO_2

Slag No. 1. - The ratios are practically the same for each solution. This indicates that the three constituents under

consideration are combined together in the slag. The slight variations that occur are to be expected due to the complex and hetrogeneous nature of the materials.

The CaO : P_2O_5 ratio is practically the same as that obtained with 2% citric acid. The difference in soluble CaO, P_2O_5 and SiO_2 between the figures obtained with any two solutions, provided there has not been reprecipitation of some of these constituents after solution from the slag, should give a more nearly correct value for the CaO : P_2O_5 : SiO_2 ratios of the compounds occurring in the slag, since the effect due to "CaO" occurring as free oxide is disposed of. The differences in soluble phosphoric oxide for adjacent solutions are so small when compared with the amount soluble in the more acid solutions that a very small experimental error in the phosphate determination may mask the true results. With regard to solutions 7 and 8 where PH of extract is 5.67 and 6.40 respectively, it is to be noted that these extracts come within the range where dicalcium phosphate, or tricalcium phosphate may be precipitated from solution. Britton (15) has shown that this does take place when solution is more alkaline that PH 5.5. Some of the ratios have been calculated.

These are given below.

Diff. between soluble constituents

		Sol.1	and	Sol. 8	give	$CaO:P_2O_5:SiO_2$=7.39:1:1.66
"	"	1	"	7	"	=7.17:1:1.73
"	"	2	"	8	"	=7.86:1:1.80
"	"	2	"	7	"	=7.91:1:1.97
"	"	1	"	5	"	=7.59:1:2.82
"	"	3	"	7	"	=7.79:1:1.92

These confirm the view that the phosphorus compounds present in this slag are silico phosphates. A mixture of silico phosphate $SiO_2:P_2O_5$ :: 1 : 1 and silico phosphate $SiO_2:P_2O_5$: : 3 : 1 would give the above ratios.

Slag No. 2.

The ratios of soluble $CaO:P_2O_5:SiO_2$ obtained with this slag are very different from those obtained with the preceding slag. They show that the calcium, silicon, and phosphorus are not all combined together.

If the apatite equivalent for calcium is taken for the phosphoric oxide from the figures obtained for molecular ratios of soluble constituents the ratios of the remaining $CaO:SiO_2$ are as follows:-

Solution 1. 2.58 : 2, 2.77 : 3, 2.74; 4, 2.75 : 5, 3.00
6, 2.92 : 7, 3.34 : 8, 3.85.

These are above the value required for dicalcium silicate but allowance is to be made for the "CaO" occurring in spinelloid material, and as free oxide. This would account also for the increased ratio observed with solutions containing less acid since the amount of "CaO" obtained from "spinels" and free oxide, relative to the amount of dicalcium silicate becoming soluble increases.

As with slag No. 1, the small differences in soluble "CaO" and "P_2O_5" with adjacent solutions compared with the actual amounts soluble render the molecular ratios calculated from these figures inaccurate. The figures obtained from widely separated solutions give more reliable results.

The PH of extracts 7 and 8 are both within the limit for precipitation of calcium phosphate.

Diff. between soluble constituents of Sol. 2 and Sol. 6 $CaO:SiO_2:P_2O_5$ 7.7:1:2.1

" 1 " 5 " 5.5:1:1.8

" 1 " 6 " 6.6:1:1.9

Apatite would require 3.3 CaO for 1 P_2O_5. The ratios of the remaining CaO : SiO_2 are

4.4 : 2.1

2.2 : 1.8

3.3 : 1.9

Acklam Ball Slag A.

The molecular ratios of $CaO:P_2O_5:SiO_2$ show variations, as in Slag No. 2, which is also a fluorspar slag. Microscopic examination has shown the presence of apatite, and if the CaO equivalent for the P_2O_5 to give apatite ratio is subtracted from the total CaO, the ratio of the remaining CaO to SiO_2 is as follows:-

Solution 1, 1.7: Solution 2, 1.6: 3, 1.6: 4, 1.6:
5, 1.7: 6, 1.7: 7, 1.8; 8, 2.0.

Consideration of the molecular formula provides an explanation for this ratio being less than 2. There is not sufficient "CaO" present to combine with all the phosphate and silica to give apatite and dicalcium silicate respectively, so that magnesium silicate is probably present in solid solution with calcium silicate.

Differences in soluble CaO, P_2O_5, and SiO_2 with solutions widely different in acidity value give molecular ratios similar to those obtained from the solubility figures.

Diff. of soluble constituents of
Sols. 1 and 6 $CaO:P_2O_5:SiO_2$ :: 6.5 : 1 : 1.9
" 1 " 5 " :: 5.79: 1 : 1.49.

With phosphate present as apatite, requiring 3.3 CaO: 1 P_2O_5, the remaining $CaO:SiO_2$ = 1.68 : 1, and 1.65 : 1 respectively.

Acklam Ball Slag C.

The molecular ratios of soluble CaO:P_2O_5: SiO_2 show, as with the other fluorspar slags examined, wide variations.

After subtracting from total soluble CaO that required by P_2O_5 figure to give phosphate as apatite, the remaining CaO gives the following ratios with SiO_2.

Solution 1, 2.0 : Sol. 2, 1.8 : 3, 1.8 : 5, 1.8; 6, 1.8 : 7, 1.8 : 8, 1.9.

indicating the presence of dicalcium silicate.

The above ratios are slightly higher than those obtained with Acklam Ball Slag, Sample A, due to the fact that % silica contained in this sample is 14, that of sample A is 15.

Comparison of Solubility of Acklam Ball Slags.

The percentage solubility figures for "CaO", "P_2O_5" and "SiO_2" with sample A are in every case lower than those obtained with sample C. The "CaO", "P_2O_5", and "SiO_2" contents of the samples are practically the same.

	% CaO	% P_2O_5	% SiO_2
(A)	46.01	17.54	15.00
(B)	45.75	18.04	14.00

The most outstanding difference between the two samples is in texture, as noted in microscopic examination. To this the difference is solubility is attributed.

Main conclusions that have been formed are

1. That no outstanding concentration of the chief constituents "P_2O_5" and "CaO" of basic slags, 1. Non-fluorspar, 2. fluorspar, is obtained on separation of slags, ground as for fertiliser use, into 5 fractionsaccording to particle size.

2. Solubility of the "P_2O_5" present in basic slags in 2% oxalic acid, under conditions of official citric acid solubility test, increases with fineness of grinding to a much greater extent than that shown with 2% citric acid.

3. That the phosphate present in fluorspar slags is soluble in 2% citric acid on repeated extraction, as shown by G. S. Robertson (7).

4. That the differences in citric acid soluble and total phosphate content noted by Sullwald (13) in samples taken from different points of the slag ball with Thomas slag are not apparent in fluorspar open hearth slags. No increase in total phosphate content is noted: increase in citric acid soluble "P_2O_5" with samples taken from the centre as compared with those from the outside of the ball is due to difference in physical state of the components of the samples.

5. That the phosphatic constituent of fluorspar slags, although the additions of fluorspar during dephosphorisation of the steel have been reduced, is apatite.

6. That the value of fluorspar slags in neutralising acidity is greater than that of a non-fluorspar slag: this property affects the solubility of the phosphoric oxide present in slags, as measured by the "citric acid test", the empirical nature of which has been demonstrated.

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Part 11.

Studies in the Uses of Basic Slags.

Introduction.

This section deals with the uses of modern basic slags as fertilisers.

Basic slags are usually classed as phosphatic fertilisers, and are graded according to "P_2O_5" content, although the other constituents, especially calcium (6) (10) have been shown to be of value.

It is now known that the feeding value of grass and other crops is largely bound up with their content of minerals, especially of phosphoric acid and lime. There is evidence (16) to show that basic slags in common with other phosphatic fertilisers affect the percentage of these and other constituents in the crops.

The object of the following work was to provide further evidence of this effect and to obtain a comparison of the fertiliser value of two basic open hearth slags of the same grade but of different citric acid solubility with reference to the "P_2O_5" present in the slags, under the soil and climatic conditions of South Ayrshire.

Previous literature.

Although since 1884, when Wrightson and Munro showed that basic slag was of use as a fertiliser, a great number of experiments (see G.S. Robertson - Basic Slags and Rock Phosphates, Camb. Univ. Press 1922; Jour. Min. Agric. N. Ireland 1927. 1; Reports of Permanent Committee on Basic Slag, Ministry of Agriculture and Fisheries 1921-1932, Nos. 1 - 10; and Artificial Fertilisers, Bulletin No. 28 Min. of Agriculture) have been carried out to demonstrate, evaluate and compare the values of slags of different properties, little attention has been paid, until recently, to the effect of applications of these on the various constituents in crops.

W. Godden (J. Agr. Sci. 1926, 16, 98) in an investigation on the mineral content of pasture grass found, on typical moorland pasture, that application of basic slag resulted in a marked increase in the percentage phosphorus and a rise in the nitrogen content of the herbage, in a sample taken about eight months after treatment. He also showed that for two adjacent fields in Aberdeenshire, on similar soil, application of slag, following that of waste lime to the previous crop, to one of the fields resulted in a marked rise in percentages of silica free ash, of each ash

constituent, and of nitrogen, and a marked drop in the percentage of fibre in the dry matter of the herbage, in samples collected six years after the last application of slag to the treated field. The other field had been sown for fourteen years and had received no fertiliser treatment. In 1929 (Permanent Committee's report 1930 No. 8) a preliminary experiment at Rothamsted on grassland repeatedly mown at different intervals throughout the season, showed small increases due to slag treatment but demonstrated that more phosphoric acid was taken up by the crop with the more soluble phosphatic fertilisers.

Detailed analyses of the yields of grass and uptake of phosphoric acid were also given for four years continued experimentation on meadow land at two centres. On a calcareous soil in Norfolk the mean ratios in yield over four years were approximately in the ratios 1 : 2 : 3 for low, medium and higher soluble slags. On an acid soil in Somerset there was a much smaller response, and the differences were too small to be regarded as well established. At both centres the P_2O_5 contents of the hay were increased by more than one half, by the two more soluble slags. It was further noted "that whether or not the greater uptake of P_2O_5 is accompanied by greater dry matter per acre it is

clear that such increased phosphoric acid contents of the total herbage may well have important effects on the nutritive value especially as other mineral elements may well be expected to show the same effects".

Experiments also showed that the difference between medium soluble and high soluble slags was less than that indicated by the citric acid solubility, and appeared to vary with the type of soil. Results of a preliminary series of pot experiments indicated that basic slag was about as effective as an equal weight of $CaCO_3$ for liming purposes. The difficulty of discriminating between the direct nutritional effect of the phosphoric acid and the indirect effect due to the basic material supplied in the slag was also noted.

Permanent Committee's report No. 9, 1931. Results of phosphatic fertiliser trials on meadow hay were given. They showed that superphosphate not only increased the yield but markedly increased the percentage of nitrogen in the herbage. At one centre superphosphate actually doubled the amount of protein per acre, and the benefit from phosphate was therefore much greater than that suggested by the yield figures alone. The gain in protein formed so large a fraction of the total gain in dry matter that the crop gained by the use of phosphates was much richer than ordinary hay, and approached

the composition of a concentrated feeding stuff. At other centres the responses in yield were smaller but the phosphoric oxide content of the hay was appreciably increased by high soluble slag. The phosphoric acid percentages in the dry matter and the total phosphoric acid in the crop per acre proved to be good criteria for distinguishing between the availability of the different phosphates, even where they gave substantially equal yields of hay. Average figures of yield of dry matter, protein and phosphoric acid showed that high soluble slag was half as effective as superphosphate, low soluble slag half as effective as high soluble slag, and mineral phosphate still less effective.

In a repeatedly mown experiment at Cockle Park on very poor grassland high soluble slag (14.92% P_2O_5, citric solubility 96.5%) gave higher P_2O_5 content of the crop than low soluble slag (15.10% P_2O_5, citric solubility 23%). The slag dressings were given at rates equivalent to 112 lb. P_2O_5 per acre.

(Permanent Committee's report 1932). In the first year of a hay experiment near Northallerton, Yorkshire, marked responses to the fertilisers were obtained. Superphosphate and high soluble slag increased the dry matter yield by almost one-half, and low soluble slag by one-fifth. There were still

greater effects on the production of protein per acre, the increases being superphosphate three-quarters, high soluble slag two thirds, and low soluble slag one-quarter. Superphosphate and high soluble slag raised the total P_2O_5 of the herbage per unit area from two to three times that on the unmanured land. About one-tenth of the P_2O_5 added was recovered in the hay crop only five months after manuring. Of three experiments on arable land begun in 1931, with swedes, the only one showing significant difference in yield was at Welshpool where high soluble slag gave higher yields than no phosphate. At the other two centres Moulton and Cundle, where the produce was analysed no appreciable difference in the P_2O_5 contents of the swedes was obtained.

Nature of Experiments.

Field experiments, during seasons 1932 and 1933 have been carried out.

(1) Experiment on grassland, mown at intervals throughout the season, 1932.

(2) Experiment on arable land with swedes, season 1932.

(3) Experiment with oats following swedes of No. 2, to test residual values of the slags, 1933.

Field Experiment Slags.

The same two slags were used in the experiments. These slags were supplied as being of the same grade but of different

solubility in citric acid, one high soluble with reference to "P_2O_5" present (hereafter referred to as Slag H), the other low soluble (Slag L.)

The chemical composition and citric acid solubility were determined. The results are given in the following tables Nos. 39 and 40.

Table No. 39. Chemical composition of Field Experiment Slags.

	(H)	(L)
% P_2O_5	14.89	15.65
% CaO	46.90	32.42
% SiO_2	10.38	13.48
% MgO	8.82	5.67
% FeO	5.34	15.20
% Fe_2O_3	5.65	4.09
% MnO	4.58	6.53
% Al_2O_3	3.33	3.75

The molecular formulae calculated from above are as follows:-

Slag H.

CaO .837
MgO .219
MnO .0646
FeO .0743

Fe_2O_3 .0354
Al_2O_3 .0327

SiO_2 .172
P_2O_5 .105

i.e. RO : R_2O_3 .057 : SiO_2 .144, P_2O_5 .088

Slag L

CaO	.578	Fe_2O_3	.0256	SiO_2	.223
MgO	.141	Al_2O_3	.0368	P_2O_5	.110
MnO	.0921				
FeO	.2115				

i.e. RO : R_2O_5 .061 : (SiO_2 .218, P_2O_5 .108)

Table No. 40. 2% Citric acid solubility (official method) of Field Experiment Slags.

Slag.	H.	L.
Reduction of acidity by 5 gm. of slag	≡ 62.3 cc N.	≡ 33.1 cc N
% Soluble "P_2O_5"	10.6	7.4
% Solubility "P_2O_5"	71.2	47.2
% Soluble "CaO"	34.5	19.2
% Solubility "CaO"	73.55	59.25

Field Experiment No. 1.

Experiment on grassland, with several cuttings.

This was a small scale experiment in which the herbage was removed by cutting with shears, during dry weather, at intervals during the growing season when the grass was in a state suitable for grazing. The results must necessarily be different from those of an actual grazing trial. They measure the amount of herbage produced, so far as uniform

cutting could be obtained with shears, and are free from the complications of selective grazing.

Centre of experiment - Auchincruive, Ayrshire.

Form - The experimental area was a rectangular strip, 2 yd. x 26 yd., divided into 13 square plots, each 2 yd. x 2 yd. numbered and treated as shown in the following plan.

2 yd.

H No.2	L 3	C 4	H 5	C 6	L 7	C 8	H 9	C 10	L 11	C 12	H 13	L 14

26 yd.

H - denotes treatment with "high citric soluble" slag.

L - " " "low " "

C - untreated.

The slags were applied on April 5, 1932, at the rate of 630 gm. per plot, i.e. at the rate of 15 cwt/acre. The herbage at that time was of old natural grass which so far as could be ascertained had not received any manurial treatment.

Examination of Soil Conditions.

Any attempt to compare fertiliser values by means of field experiments is necessarily incomplete if it does not take soil conditions into account. Accordingly, before the slags were applied, the soil was sampled in a number of places in

the usual way, due regard being paid to ensuring that the bulk sample was, as far as possible, representative. The analytical results are tabulated in Table No. 41.

Table No. 41. Analysis of soil sample from pasture plots.

Mechanical analysis	%
Coarse sand	33.94
Fine Sand	45.84
Silt	6.11
Clay	9.14
Moisture	1.40
Loss on solution	1.50
Difference	2.33
Chemical analysis	**%**
Loss on ignition	5.8
P_2O_5 soluble in HCl	.082
P_2O_5 soluble in 2% citric acid	.0113
PH (water suspension)	5.03
PH ($CaCl_2$ suspension)	4.25
"Lime Requirement"	
(Hardy and Lewis Method)	.245 %
(Hutchison and McLennan)	.170 %

Weather conditions during experiment.

Although no attempt is made in this work to discuss in detail the correlation between productivity and weather conditions, due attention was paid to keeping an account of the weather data during the experiment. The readings were taken at the Meteorological Station Auchincruive, within a short distance of the experimental centre.

In the reports, given later, dry bulb and wet bulb readings refer to thermometers in screen four feet above the ground. Sunshine is as recorded by the Campbell-Stokes recorder.

Herbage.

Chemical composition and yields.

The herbage cut from each plot was weighed as cut. A sample of each, after careful oven drying at 80°C to give dry matter content, was ground to a fine powder and examined quantitatively for ash, ash insoluble in hydrochloric acid, acid soluble in hydrochloric acid, CaO, K_2O, Na, N, and P_2O_5. Results of these analyses are given on the dry matter basis.

It was not possible by the methods employed to cut the herbage in a dry condition (to give comparative dry matter figures) and deal with the samples, for dry matter determination, from all of the plots in one day so that

variations in dates of cutting and consequently in growing periods between cuts occur.

The results obtained for the herbage collected from the individual plots, together with the meteorological data, are given in one table, so that seasonal variations in chemical composition and productivity, and relation with weather conditions are shown.

Table No. 42. Herbage composition and yields, with meteorological data Plot No. 2.

Slag H.

Date of cutting.	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO.	% K_2O.	% Na.	% N.	% P_2O_5
6/5/32	31.7	8.00	4.08	3.92	.893	1.03	.133	2.17	.678
27/5/32	24.7	8.19	2.92	5.28	.935	1.93	.226	2.48	.745
29/6/32	30.7	8.17	2.31	5.86	1.40	1.75	.291	2.45	.612
4/8/32	23.9	8.79	2.23	6.56	1.39	2.07	.253	2.80	.806
20/9/32	24.4	8.20	2.52	5.68	1.56	1.73	.267	2.49	.794

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	47.31	3.79	1.93	1.86	.422	.486	.0629	1.03	.321
2nd cut	99.28	8.13	2.90	5.24	.928	1.92	.223	2.46	.740
3rd cut	115.1	9.40	2.66	6.74	1.612	2.01	.335	2.45	.705
4th cut	188.1	15.92	4.04	11.88	2.511	3.75	.458	5.08	1.47
5th cut	300.1	24.60	7.56	17.04	3.46	5.19	.800	7.46	2.38

Meteorological data.	Average.		Temperatures °F.			Rainfall	Sunshine
	No. of days.	Dry Bulb.	Wet bulb.	Grass Min.	1ft. in ground	(inches)	(hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	21	51.6	47.6	37	51.4	2.51	107.2
" 2nd " " 3rd "	33	58.0	52.9	41	58.2	1.51	216.9
" 3rd " " 4th "	36	59.5	55.9	48	60.3	4.02	127.9
" 4th " " 5th "	47	61.1	55.6	46	60.0	5.59	177.4

Table No. 43. Herbage composition and yields, with meteorological data Plot No. 3.

Slag L.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	32.05	7.39	4.35	3.04	.982	1.15	.145	2.06	.692
27/5/32	24.05	7.47	2.27	5.19	.956	2.04	.258	2.42	.837
29/6/32	34.30	8.20	2.65	5.55	1.242	1.50	.235	2.03	.567
4/8/32	27.85	8.67	2.59	6.08	1.213	1.95	.230	2.42	.729
20/9/32	27.00	8.25	3.03	5.22	1.048	1.68	.238	2.25	.807

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	64.3	4.75	2.80	1.95	.631	.740	.0932	1.33	.631
2nd cut	87.5	6.54	1.99	4.55	.837	1.785	.226	2.11	.837
3rd cut	88.8	7.28	2.35	4.93	1.104	1.332	.209	1.80	1.104
4th cut	166.5	14.44	4.31	10.13	2.019	3.246	.383	4.03	2.019
5th cut	214.7	17.71	6.51	11.19	2.25	3.607	.510	4.82	2.25

Meteorological data	No. of days.	Average Dry bulb.	Temperatures °F Wet bulb.	Grass Min.	1ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	21	51.6	47.6	37	51.4	2.51	107.2
" 2nd " " 3rd "	33	58.0	52.9	41	58.2	1.51	216.9
" 3rd " " 4th "	36	59.5	55.9	48	60.3	4.02	127.9
" 4th " " 5th "	47	61.1	55.6	46	60.0	5.59	177.4

Table No. 44. Herbage composition and yields, with meteorological data Plot No. 4.

Untreated.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	32.60	6.00	3.47	2.53	.508	.819	.098	1.99	.480
27/5/32	24.50	6.47	1.39	5.08	.846	1.93	.310	2.48	.600
29/6/32	29.10	7.90	2.33	5.57	1.172	1.73	.260	2.23	.526
4/8/32	25.85	7.76	2.01	5.75	1.028	1.99	.243	2.53	.532
20/9/32	29.80	7.48	2.47	5.01	.800	1.74	.239	2.23	.547

Yield in grams -	Dry matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	113.4	6.81	3.93	2.87	.576	.929	.111	2.25	.544
2nd cut	66.6	4.31	.926	3.39	.564	1.285	.207	1.65	.399
3rd cut	114.1	9.01	2.66	6.36	1.338	1.973	.297	2.55	.600
4th cut	151.5	11.75	3.05	8.70	1.557	3.015	.368	3.84	.806
5th cut	191.2	14.29	4.71	9.58	1.53	3.326	.457	4.26	1.014

Meteorological data	Average No. of days.	Dry bulb	Temperatures °F Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	21	51.6	47.6	37	51.4	2.51	107.2
" 2nd " " 3rd "	33	58.0	52.9	41	58.2	1.51	216.9
" 3rd " " 4th "	36	59.5	55.9	48	60.3	4.02	127.9
" 4th " " 5th "	47	61.1	50.9	46	60.0	5.59	177.4

Table No. 45. Herbage composition and yields, with meteorological data Plot No. 5.

H.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	32.25	7.76	4.83	2.93	.778	.745	.0735	2.00	.742
27/5/32	24.35	7.59	2.50	5.09	1.067	1.92	.222	2.42	.717
29/6/32	29.65	9.26	3.56	5.70	1.230	1.61	.234	2.16	.569
4/8/32	24.05	8.44	2.13	6.31	1.346	2.09	.246	2.73	.721
20/9/32	22.90	8.73	3.54	5.18	1.015	1.69	.202	2.34	.826

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	68.2	5.30	3.29	2.00	.531	.508	.0501	1.36	.506
2nd cut	95.0	7.20	2.37	4.83	1.014	1.824	.211	2.30	.681
3rd cut	126.6	11.72	4.51	7.22	1.567	2.038	.296	2.74	.720
4th cut	189.8	16.02	4.04	11.97	2.555	3.968	.467	5.18	1.370
5th cut	300	26.18	10.63	15.55	3.045	5.079	.606	7.03	2.478

Meteorological data	No. of days	Average Dry bulb.	Temperatures °F. Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	21	51.6	47.6	37	51.4	2.51	107.2
" 2nd " " 3rd cut	33	58.0	52.9	41	58.2	1.51	216.9
" 3rd " " 4th cut	36	59.5	55.9	48	60.3	4.02	127.9
" 4th " " 5th cut	47	61.1	50.9	46	60.0	5.59	177.4

Table No. 46. Herbage composition and yields, with meteorological data Plot No. 6.

Untreated.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	30.40	6.75	2.75	4.00	.667	1.51	.0859	2.13	.525
27/5/32	25.70	7.66	2.30	5.36	.765	2.35	.238	2.46	.556
29/6/32	27.90	8.33	2.52	5.81	1.123	1.57	.263	2.03	.490
4/8/32	25.85	8.42	2.39	6.03	.982	2.25	.246	2.37	.610
22/9/32	32.15	8.89	3.47	5.42	.800	1.75	.211	2.38	.574

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	75.3	5.08	2.07	3.01	.502	1.14	.0647	1.60	.395
2nd cut	109.2	8.36	2.51	5.85	.836	2.57	.260	2.69	.607
3rd cut	106.9	8.91	2.70	6.21	1.200	1.67	.281	2.17	.524
4th cut	144.2	12.14	3.45	8.69	1.416	3.25	.355	3.42	.880
5th cut	249.8	22.21	8.67	13.55	1.998	4.37	.526	5.95	1.434

Meteorological data	Average No. of days.	Temperatures °F Dry bulb.	Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	21	51.6	47.6	37	51.4	2.51	107.2
" 2nd cut to 3rd cut	33	58.0	52.9	41	58.2	1.51	216.9
" 3rd cut to 4th cut	36	59.5	55.9	48	60.3	4.02	127.9
" 4th cut to 5th cut	49	60.5	55	45.1	59.8	5.61	192.7

Table No. 47. Herbage composition and yields, with meteorological data Plot No. 7.

Slag L.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	33.2	8.39	4.33	4.06	.924	1.046	.099	1.94	.717
27/5/32	25.05	7.72	2.50	5.22	.939	1.95	.216	2.49	.753
7/7/32	30.45	9.39	2.91	6.48	1.400	1.70	.268	2.59	.722
13/8/32	27.00	9.22	2.64	6.58	1.350	2.08	.261	2.78	.814
22/9/32	27.65	9.68	4.02	5.66	1.139	1.68	.228	2.68	.881

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	116.5	9.77	5.04	4.73	1.08	1.22	.115	2.26	.835
2nd cut	137.8	10.64	3.44	7.20	1.29	2.69	.298	3.43	1.039
3rd cut	145.2	13.63	4.22	9.42	2.03	2.47	.388	3.76	1.048
4th cut	298.4	27.52	7.88	19.64	4.04	6.20	.776	8.28	2.43
5th cut	261.4	25.30	10.51	14.79	2.98	4.38	.595	7.01	2.30

Meteorological data.

	No. of days	Average Dry Bulb.	Temperatures °F Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	21	51.6	47.6	37	51.4	2.51	107.2
" 2nd " " 3rd "	41	57.1	52.1	43	57.1	2.58	243.9
" 3rd " " 4th "	37	60.0	56.5	49	60.7	3.66	127.9
" 4th " " 5th "	40	60.1	54.2	44	59.4	5.10	165.7

Table No. 48. Herbage composition and yields, with meteorological data Plot No. 8.

Untreated.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	33.1	6.78	3.53	3.25	.538	1.12	.107	1.95	.574
27/5/32	23.4	6.55	1.63	4.92	.829	2.22	.263	2.38	.670
7/7/32	31.3	8.80	2.79	6.01	1.205	1.80	.238	2.34	.571
13/8/32	27.95	9.46	3.28	6.18	1.057	2.13	.242	2.42	.610
22/9/32	29.82	9.55	3.85	5.70	.850	1.96	.216	2.43	.651

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	133.8	9.06	4.71	4.34	.720	1.50	.143	2.60	.687
2nd cut	101.4	6.64	1.65	4.99	.840	2.25	.267	2.42	.681
3rd cut	132.3	11.63	3.70	7.95	1.594	2.38	.315	3.09	.755
4th cut	154.8	14.65	5.08	9.57	1.636	3.30	.375	3.75	.944
5th cut	161.6	15.43	6.22	9.21	1.374	3.17	.349	3.92	1.052

Meteorological data	Average No. of days	Average Dry bulb	Temperatures °F Wet bulb	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	21	51.6	47.6	37	51.4	2.51	107.2
" 2nd " " 3rd "	41	57.1	52.1	43	57.1	2.58	243.9
" 3rd " " 4th "	37	60.0	56.5	49	60.7	3.66	127.9
" 4th " " 5th "	40	60.1	54.2	44	59.4	5.10	165.7

Table No. 49. Herbage composition and yields, with meteorological data Plot No. 9.

Slag H.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	29.30	7.99	3.89	4.10	.839	1.33	.084	2.22	.676
30/5/32	24.80	8.31	2.89	5.42	1.03	2.24	.235	2.46	.711
7/7/32	29.00	9.81	3.62	6.19	1.42	1.66	.253	2.45	.780
13/8/32	22.20	9.49	2.68	6.82	1.57	2.04	.258	2.83	.850
22/9/32	24.97	10.29	4.44	5.84	1.19	1.68	.243	2.67	.951

Yield in grams -	Dry matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	103.5	8.27	4.03	4.24	.869	1.38	.087	2.29	.70
2nd cut	194.2	16.14	5.61	10.52	2.00	4.35	.456	4.78	1.50
3rd cut	132.2	12.96	4.78	8.18	1.88	2.20	.334	3.24	1.03
4th cut	242.4	23.01	6.49	16.52	3.80	4.94	.625	6.85	2.06
5th cut	273.4	28.11	12.15	15.97	3.25	4.59	.662	7.29	2.60

Meteorological data	No. of days	Average Dry bulb.	Temperatures °F Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	24	51.9	48.0	38	51.7	2.56	115.7
" 2nd " " 3rd "	38	58.8	53.8	42	58.9	2.33	235.4
" 3rd " " 4th "	37	60.0	56.5	49	60.7	3.66	127.9
" 4th " " 5th "	40	60.1	54.2	44	59.4	5.10	165.7

Table No. 50. Herbage composition and yields, with meteorological data Plot No. 10.

Untreated.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
11/5/32	29.25	6.01	2.32	3.69	.672	1.23	.0955	2.07	.534
30/5/32	22.85	6.83	1.57	5.26	.910	2.05	.290	2.32	.657
7/7/32	29.80	9.08	3.41	5.68	1.19	1.57	.263	2.38	.587
13/8/32	24.35	9.10	3.50	5.60	.978	1.84	.229	2.44	.655
22/9/32	26.08	10.34	4.86	5.48	.842	1.81	.203	2.53	.695

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	124	7.45	2.88	4.57	.833	1.53	.118	2.57	.662
2nd cut	135.3	9.24	2.12	7.12	1.23	2.77	.392	3.13	.889
3rd cut	132.9	12.07	4.53	7.54	1.58	2.09	.350	3.16	.780
4th cut	213.5	19.42	7.47	11.95	2.09	3.93	.489	5.21	1.398
5th cut	172.4	17.82	8.38	9.44	1.45	3.12	.350	4.37	1.198

Meteorological data	Average No. of days.	Dry bulb.	Temperatures °F Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshi (hours)
From application of slags to 1st cut	36	46.1	42.2	30	46.1	2.79	213.8
" 1st cut to 2nd cut	19	53.1	49.6	41	52.5	2.11	74.1
" 2nd " " 3rd "	38	58.8	53.8	42	58.9	2.33	235.4
" 3rd cut " 4th "	37	60.0	56.5	49	60.7	3.66	127.9
" 4th " " 5th "	40	60.1	54.2	44	59.4	5.10	165.7

Table No. 51. Herbage composition and yields, with meteorological data Plot No. 11.

Slag L.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
11/5/32	27.75	7.36	3.58	3.78	.793	.977	.129	2.02	.658
30/5/32	21.55	8.26	2.80	5.46	.939	1.80	.321	2.50	.791
7/7/32	29.70	10.11	3.97	6.13	1.354	1.45	.279	2.39	.744
13/8/32	20.90	9.89	3.98	5.91	1.17	1.69	.256	2.49	.872
22/9/32	24.00	10.30	4.75	5.55	1.08	1.62	.247	2.54	.904

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	208.9	15.39	7.48	7.90	1.66	2.04	.269	4.23	1.38
2nd cut	158.0	13.05	4.42	8.63	1.49	2.84	.507	3.95	1.25
3rd cut	145.0	14.65	5.76	8.89	1.96	2.10	.405	3.47	1.08
4th cut	266.7	26.37	10.61	15.75	3.11	4.55	.683	6.64	2.33
5th cut	215.6	22.20	10.23	11.97	2.33	3.49	.533	5.48	1.95

Meteorological data	Average No. of days.	Average Dry bulb.	Temperatures °F Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	36	46.1	42.2	30	46.1	2.79	213.8
" 1st cut to 2nd cut	19	53.1	49.6	41	52.5	2.11	74.1
" 2nd " " 3rd "	38	58.8	53.8	42	58.9	2.33	235.4
" 3rd " " 4th "	37	60.0	56.5	49	60.7	3.66	127.9
" 4th " " 5th "	40	60.1	54.2	44	59.4	5.10	165.7

Table No. 52. Herbage composition and yields, with meteorological data Plot No. 12.

Untreated.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
11/5/32	30.5	6.15	2.64	3.50	.618	1.23	.157	2.02	.544
30/5/32	22.85	7.39	2.61	4.78	.722	1.88	.270	2.48	.713
7/7/32	29.6	9.58	3.75	5.83	1.19	1.58	.282	2.33	.586
13/8/32	23.00	9.60	3.74	5.86	1.07	1.85	.255	2.53	.735
22/9/32	25.58	9.51	4.17	5.34	.883	1.77	.224	2.41	.682

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	168.4	10.35	4.45	5.90	1.04	2.08	.265	3.40	.916
2nd cut	165.0	12.22	4.32	7.91	1.20	3.11	.447	4.10	1.18
3rd cut	133.2	12.76	5.00	7.77	1.59	2.11	.376	3.11	.781
4th cut	184.2	17.69	6.89	10.80	1.98	3.41	.470	4.67	1.35
5th cut	203.3	19.32	8.48	10.85	1.80	3.60	.456	4.90	1.39

Meteorological data	Average No. of days.	Average Dry bulb.	Temperatures °F Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	36	46.1	42.2	30	46.1	2.79	213.8
" 1st cut to 2nd cut	19	53.1	49.6	41	52.5	2.11	74.1
" 2nd cut to 3rd cut	38	58.8	53.8	42	58.9	2.33	235.4
" 3rd cut to 4th cut	37	60.0	56.5	49	60.7	3.66	127.9
" 4th cut to 5th cut	40	60.1	54.2	44	59.4	5.10	165.7

Table No. 53. Herbage composition and yields, with meteorological data Plot No. 13.

Slag H.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
11/5/32	30.5	7.43	3.22	4.21	.961	1.06	.143	1.99	.635
30/5/32	22.65	8.48	2.76	5.71	1.34	1.88	.276	2.53	.790
7/7/32	27.8	10.03	3.54	6.49	1.55	1.69	.271	2.36	.724
13/8/32	19.95	10.59	3.80	6.78	1.46	1.92	.262	2.72	.952
22/9/32	22.6	9.83	3.91	5.92	1.25	1.72	.252	2.63	.909

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	178.4	13.28	5.76	7.52	1.72	1.90	.255	3.55	1.13
2nd cut	186.2	15.79	5.14	10.64	2.49	3.50	.514	4.70	1.47
3rd cut	132.0	13.24	4.68	8.57	2.04	2.23	.358	3.11	.956
4th cut	280.6	29.70	10.67	19.03	4.09	5.39	.735	7.64	2.67
5th cut	269.6	26.51	10.54	15.96	3.36	4.64	.679	7.10	2.45

Meteorological data	Average No. of days.	Dry bulb	Temperatures °F Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	36	46.1	42.2	30	46.1	2.79	213.8
" 1st cut to 2nd cut	19	53.1	49.6	41	52.5	2.11	74.1
" 2nd " " 3rd "	38	58.8	53.8	42	58.9	2.33	235.4
" 3rd " " 4th "	37	60.0	56.5	49	60.7	3.66	127.9
" 4th " " 5th "	40	60.1	54.2	44	59.4	5.10	165.7

Table No. 54. Herbage composition and yields, with meteorological data Plot No. 14.

Slag L.

Date of cutting	% Dry Matter	% Ash	% Insoluble Ash	% Soluble Ash	% CaO	% K_2O	% Na.	% N.	% P_2O_5
6/5/32	30.55	9.16	4.71	4.45	1.02	1.06	.110	2.04	.754
30/5/32	21.80	8.62	3.45	5.17	.969	1.98	.241	2.55	.787
7/7/32	28.00	9.54	3.38	6.15	1.36	1.63	.263	2.40	.706
13/8/32	19.00	9.58	2.66	6.91	1.50	1.97	.263	2.76	.905
22/9/32	20.37	10.09	3.69	6.40	1.30	1.77	.253	2.93	.813

Yield in grams -	Dry Matter	Ash	Insoluble Ash	Soluble Ash	CaO	K_2O	Na.	N.	P_2O_5
1st cut	129.4	11.85	6.09	5.76	1.32	1.38	.142	2.64	.98
2nd cut	198.6	17.11	6.84	10.27	1.92	3.93	.479	5.07	1.56
3rd cut	135.0	12.87	5.57	8.31	1.84	2.20	.355	3.24	.95
4th cut	310.7	29.75	8.28	21.48	4.66	6.12	.817	8.57	2.81
5th cut	300.9	30.35	11.09	19.26	3.91	5.32	.760	8.80	2.45

Meteorological data	Average No. of days	Average Dry bulb.	Temperatures °F. Wet bulb.	Grass Min.	1 ft. in ground	Rainfall (inches)	Sunshine (hours)
From application of slags to 1st cut	31	45.9	42.3	31	45.7	2.34	172.2
" 1st cut to 2nd cut	24	51.9	48.0	38	51.7	2.56	115.7
" 2nd " " 3rd "	38	58.8	53.8	42	58.9	2.33	235.4
" 3rd " " 4th "	37	60.0	56.5	49	60.7	3.66	127.9
" 4th " " 5th "	40	60.1	54.2	44	59.4	5.10	165.7

Average Yields.

Average yields per plot, according to treatment, have been calculated. These are tabulated in Table No. 55.

Table No. 55. Average yields, in grams per plot.

	Slag H.	Slag L.	Untreated.
Fresh herbage	3584	3680	2687
Dry Matter	883	912.5	708
Ash	78.8	82.8	59.7
Insoluble Ash	28.4	31.1	22.1
Soluble Ash	50.4	51.7	37.6
CaO	10.8	10.6	6.5
K_2O	15.5	15.4	12.8
Na.	2.05	2.14	1.62
N.	21.9	22.7	17.0
P_2O_5	6.98	7.24	4.37

These results show that under the conditions of the experiment an increased yield, for the constituents determined, has been obtained in every case by the application of the basic slags. The increase of the treated plots over the untreated from the average yield figures are given in Table No. 56 as percentages of the average untreated plot yield.

Table No. 56. Average increase in productivity due to slags.

	Slag H. %	Slag L. %
Fresh cut herbage	33.4	37.0
Dry Matter	24.7	28.8
Ash	32.0	38.6
Insoluble Ash	28.5	40.7
Soluble Ash	34.0	37.5
CaO	66.2	63.0
K_2O	21.1	20.3
Na.	26.6	32.1
N.	28.8	33.5
P_2O_5	59.7	65.6

Discussion of Results.

These results show that within six months of treatment under noted conditions both slags have given an increased yield of herbage approximately one-third the yield of the untreated plot. While the limitations of such an experiment and the difficulty of interpreting the results, which represent an equilibrium set up as a result of the different actions of the slags on the various species of the herbage, which may be regarded as a mixture of competing crops, are realised, it would appear from the results of table No. 56 that the

two slags in question are practically of equal value. Where the figure for any of the constituents determined exceeds that for fresh cut herbage, it indicates an increase of that constituent in the herbage; where it is less it means that no increase has been obtained but that the increased yield is due to greater growth brought about by the fertiliser treatment. Thus slag H has increased the CaO, P_2O_5, and to a very slight extent the soluble as N. content, while slag L has increased the P_2O_5, CaO, and to a lesser extent the insoluble ash, total ash, and soluble ash content. The increase in the yield of the other constituents is due to increased growth.

The comparative effectiveness of the slags as fertilisers in providing CaO and P_2O_5, as judged by the recovery values, calculated from the average figures is

Slag L CaO 2%. P_2O_5 2.91%

Slag H. CaO 1.46% P_2O_5 2.78%.

This does not agree with the availability as shown by citric solubility test. Similar results with slags showing so-called intermediate solubility i.e. 40 - 80% have been reported. (Basic slag Committee's reports Nos. 5, 7, 8.)

Field Experiment No. 2.

Experimental Crop.

Roots crops are very sensitive to phosphatic fertilisers (17), and are therefore likely to bring any differences in the effectiveness. Of these Swedes stand high in the lists of crops showing sensitiveness to phosphate starvation, responsiveness to additions of phosphate, and ability to obtain phosphorus from relatively insoluble phosphates. They were therefore selected as the experimental crop in this case, although they have the disadvantage of a fairly long growing period and are thus not very suitable as a means of measuring the rapidity of action.

Location of Experiment.

To aid in the selection of an experimental centre, where the soil was deficient in phosphate, and would thus be likely to respond to treatment and to show differences, following treatment with slags of different properties, the Records of the Soil Survey and Advisory Staff of the West of Scotland Agricultural College were examined. This examination showed that for 292 samples of heavy loam soils of South Ayrshire, suitable for Swede growing, the average lime requirement was .26% (Hardy's Method). This was taken as being fairly representative of South Ayrshire soils, and it was attempted

to obtain a centre where the soil gave approximately the same conditions in this respect. The most suitable centre obtainable was at Friarland Farm, 2½ miles south east of Ayr, where, according to the soil record, the lime requirement was .30. The soil was also deficient in phosphate.

Soil conditions.

The soil was sampled in the usual way at the beginning of the experiment. The analytical results are given in Table No. 57.

Table No. 57. Analysis of soil sample - Friarland Experiment.

Mechanical Analysis	%
Coarse sand	14.46
Fine sand	44.80
Silt	21.33
Clay	11.84
Moisture	4.12
Loss on solution	2.23
Difference	1.22

FRIARLAND, EXPERIMENT CENTRE.

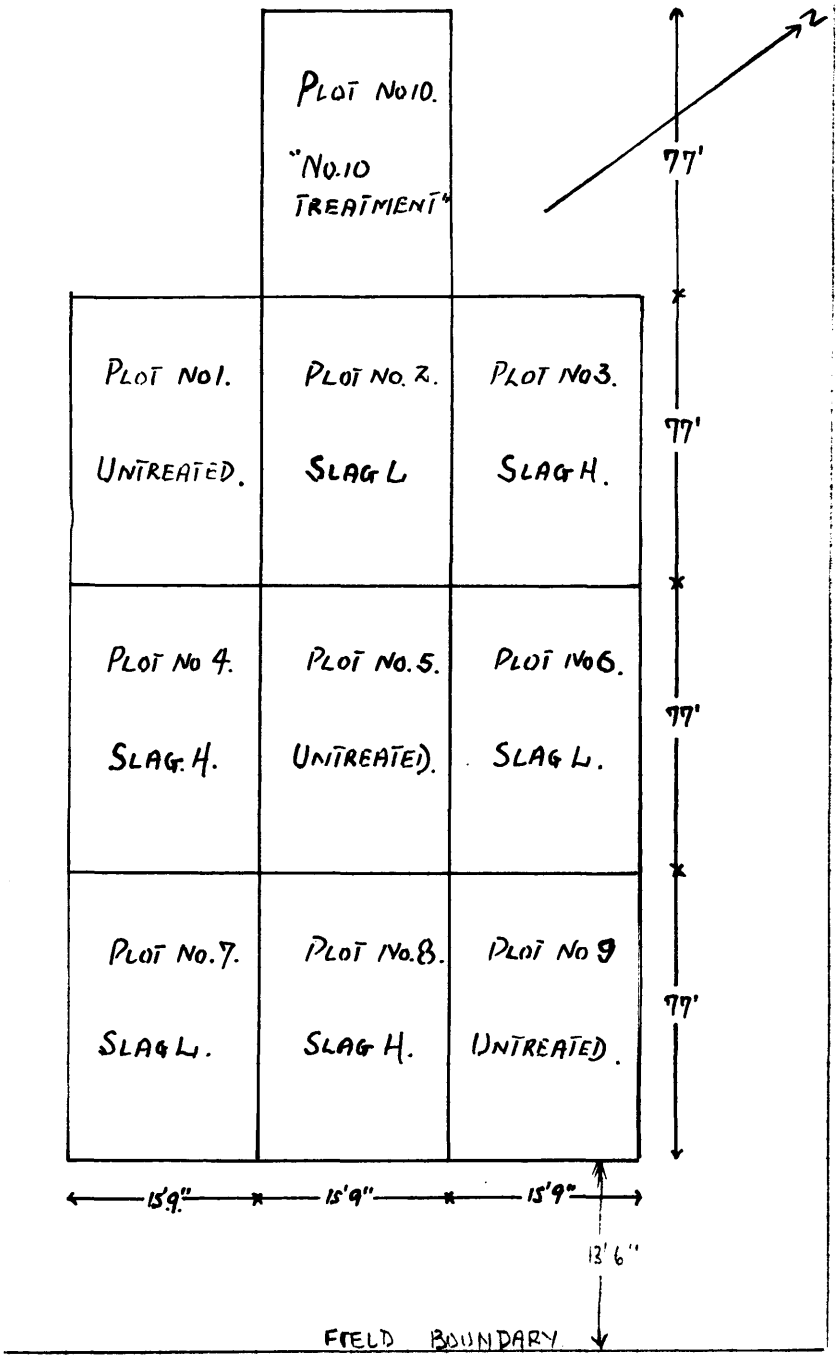


Table No. 57. (Contd.)

Chemical Analysis	%
Loss on ignition	9.8
"Lime requirement" (Lewis and Hardy)	.366
(Hutchison and McLennan)	.250
P_2O_5, HCl soluble	.232
P_2O_5, .2% Citric acid soluble	.009

PH water suspension 5.3

PH $CaCl_2$ suspension 4.5

P_2O_5 (Kirsanov) - Highly deficient.

No manurial treatment had been given for at least five years.

Form of Experiment.

The plots were laid out in the form of a Latin square, each treatment being replicated three times. The arrangement of the plots was as shown in plan on the opposite page.

An additional plot No. 10, was later included to compare the results obtained with the farmer's manurial scheme with those of the slag treated plots.

Each plot was 77 ft. x 15 ft. 9 in. (7 drills).

Treatment.

Plots No. 1, 5, 9 - Untreated.

" 2, 6, 7 - "Low citric soluble" slag 42 lb.per plot.

" 3, 4, 8 - "High " " " " " "

This heavy dressing of slag (13½ cwt./ acre) was given since no farmyard manure was being applied. The rate of application of "P_2O_5" was therefore

from "Low citric soluble slag" 235.5 lb. per acre.

from "High citric soluble slag" 224.7 lb. per acre.

The slags were sown in the drill 11/5/32.

Plot No. 10 received high grade basic slag at the rate of 8 cwt/acre, sown on ploughing and wrought in; a light dressing of farmyard manure; 30% superphosphate at rate of 3 cwt/acre and ammonium sulphate at rate of 1½ cwt/acre.

Crop details.

The seed, Inglis' Best of All, was sown 11/5/32, in drills 27 inches wide.

The plants were singled out and harvested according to the usual farm practice methods.

Weather conditions.

Meteorological data, recorded at Auchincruive Station 3 miles distant, approximately 30 feet below the level of the experimental centre, which is 150 above sea level, relative

to this experiment was

Rainfall. 11th May to 13th December - 24 inches.

Sunshine. 11th May to 25th September (no record available for interval 25th to 30th September) and 1st October to 13th December - 752 hours.

Plot Yields. - The yield of bulbs from each plot was measured by weighing on 13th December, 1932. Detailed results are given in the following Table No. 58.

Table No. 58. Root yields - Bulbs.

Plot No.	Yield - lb/plot	Tons/acre.
1	668	10.71
2	1964	31.49
3	1827	29.30
4	1925	31.30
5	1012	16.23
6	1758	28.19
7	1904	30.53
8	1662	26.65
9	269	4.31
10	1792	28.73

The average yields in tons/acre according to treatment are Untreated 10.42, Slag L 30.06, Slag H 29.08.

Discussion of results.

The yields from the control plots show a wide variation. It is also noted that although the plots dressed with slag give nearly equivalent yields, plots No. 6 and 8 nearest the corner of the field where control plot No. 9 gave only 269 lb are both below the average result for each treatment. This "corner effect" is probably due to soil variation. From the results it would seem that one plot of each treatment, control, slag L, slag H are affected. The average increase over the mean yield for the untreated plots is practically the same with the two slags.

Increase due to Slag L 19.6 tons per acre.
" " " H 18.7 " " "

The relation between the increases is similar to that obtained in Experiment No. 1, for herbage.
It is noteworthy that the average yield from plots receiving slag only is slightly better than the yield from plot No. 10.

Chemical composition of the Swedes.

To test the effect of the treatment with basic slags on the composition of the bulbs it was necessary to take samples for analysis.

Sampling of Swede bulbs.

This could have been carried out by taking a number of bulbs

sufficient to give a representative sample. There is however a great difference between material required to give a representative sample and that required for chemical analysis, and this method was considered unsuitable.

The process of sampling by taking small portions of a number of bulbs is complicated, it having been found that in the bulb the solids are distributed unevenly.

Fruwirth (18) has shown that the bark has a higher dry matter figure than the other tissues. He recommends the method of cutting a longtitudinal sector, and this method has developed so that cutting and pulping of the sample are simultaneous.

Wood and Berry (19) and Hendrick (20) have found that the flesh of the peripheral region was richest, and that the dry matter content diminished towards the centre, in transverse sections.

Wood and Berry cored horizontally through the greatest diameter. Hendrick cored diagonally.

Sansome (21) found that the southern portion of the bulb was richer in dry matter than the northern. He recommended horizontal coring in a north-south direction to minimise the error due to asymmetrical growth.

Davey (22) has confirmed Sansome's work. He found that there was little difference in accuracy between the coring methods.

The relation in dry matter value of horizontal cores, diagonal cores and whole bulbs was approximately 95 : 97 : 100 respectively. He estimated the coefficient of variability as about 1% of the dry matter value for either coring method.

To obtain a comparison of these methods when the bulbs were sampled in the field, the bulbs were sampled according to the following scheme. In each case 50 cores or slices were taken.

Plots 1 - 10. - Diagonal cores through centre in a north and south direction so far as could be ascertained from the shape of the bulbs. Sample Nos. 1 - 10.

Plots 1 - 3. Horizontal cores, through the centre, in a north and south direction. Samples Nos. 1A, 2A, and 3A.

Plots 4 - 6. Longitudinal wedge shaped sectors. Sample Nos. ivB, vB, ViB.

Plots 7 - 9. Horizontal cores, through greatest diameter. Sample Nos. 70, 80, 90.

The dry matter, ash, CaO, P_2O_5 and nitrogen contents were determined in each sample. The following table No. 59 gives the results obtained. CaO, P_2O_5, ash and nitrogen figures are given as the dry matter basis.

Table No. 59. Chemical composition of Swede bulbs.

Sample No.	% Dry Matter	% Nitrogen	% Ash	% CaO	% P_2O_5
1	10.57	2.03	4.20	.406	.280
1A	10.22	1.91	4.66	.379	.301
2	9.68	1.69	4.73	.435	.492
2A	9.76	1.67	4.49	.405	.528
3	10.17	1.59	4.77	.450	.584
3A	9.94	1.59	4.51	.419	.610
4	9.4	1.78	4.73	.440	.581
4B	9.39	1.95	5.12	.516	.633
5	9.88	1.90	4.62	.396	.329
5B	9.91	2.21	5.04	.476	.326
6	9.73	1.55	4.29	.424	.487
6B	9.57	1.58	4.70	.478	.511
7	9.49	1.73	4.57	.429	.535
7D	9.67	1.71	4.25	.390	.525
8	9.47	1.71	4.50	.433	.538
8D	9.69	1.70	4.33	.415	.577
9	10.36	1.93	3.96	.379	.249
9D	10.66	1.94	4.07	.358	.277
10	9.89	1.90	5.36	.386	.346

The dry matter, ash, CaO, N, P_2O_5 yields in lb. per acre are tabulated in Table No. 60. These results show the variations obtained by the different methods of sampling.

Table No. 60. Yield figures of Swede constituents.

Sample No.	Dry Matter	Ash	Nitrogen	CaO	P_2O_5
1	2536	106.5	51.5	10.29	7.09
1A	2451	114.2	46.8	9.28	7.38
2	6828	322.8	115.7	29.73	33.61
2A	6880	308.9	114.7	27.88	36.31
3	6674	318.0	105.8	30.00	38.97
3A	6519	294.0	103.9	27.30	39.78
4	6588	311.9	117.1	28.98	38.29
4B	6577	336.5	127.9	33.95	41.59
5	3591	165.7	68.1	14.22	11.82
5B	3598	181.4	79.3	17.14	11.74
6	6138	263.5	95.4	26.01	29.92
6B	6040	283.7	95.3	28.89	30.85
7	6489	296.6	112.4	27.86	34.69
7D	6612	280.9	112.9	25.76	34.73
8	5649	254.3	96.7	24.47	30.40
8D	5782	250.3	98.3	23.92	33.34
9	1002	39.65	19.3	3.80	2.50
9D	1030	41.96	19.9	3.69	2.86
10	6366	341	121.2	24.6	22.05

Discussion of Results.

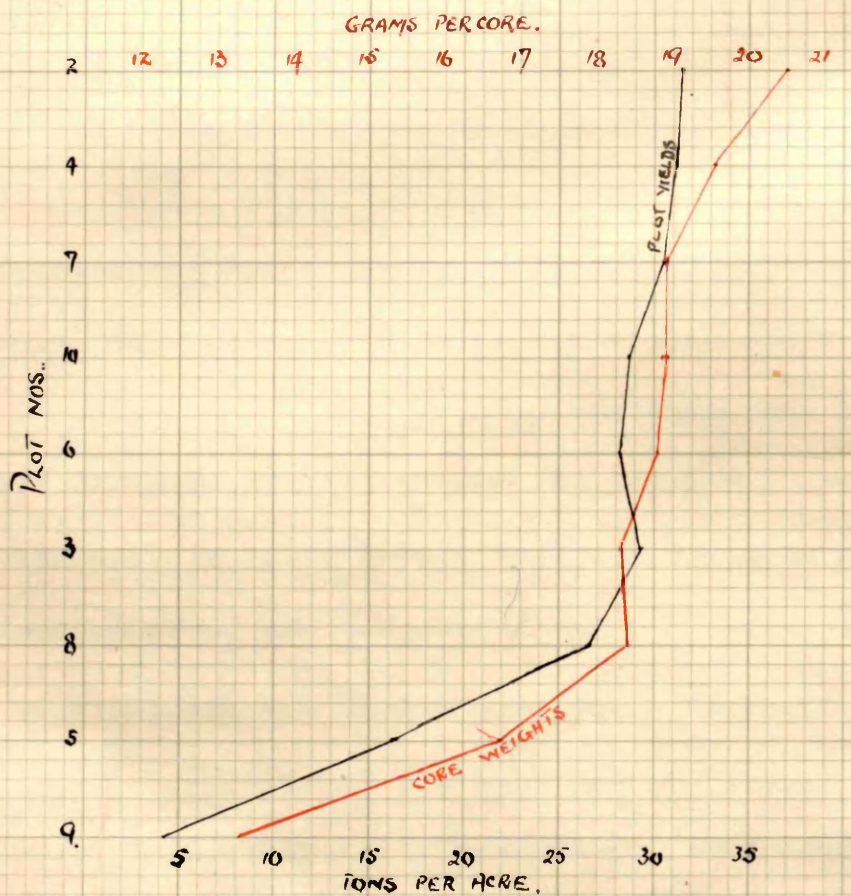
Dry matter figures for samples from plots Nos. 1, 2 and 3 show variations according to the method of sampling as noted by Davey (22). In one case the figure obtained is outside the limit suggested by Davey. He gave relative figures for diagonal and horizontal cores 97 : 95 with 1% variation in each method. In plot No. 2 the dry matter figure by horizontal coring exceeds that of horizontal cores by approximately .8%.

The dry matter figures for diagonal cores and longitudinal sectors from plots Nos. 4 - 6 agree very well. The greatest difference is approximately 1.6%.

With plots Nos. 7 - 9 the dry matter figures obtained from cores through greatest diameter exceed those of diagonal coring in each case. This is probably due to concentration of solids in transverse sections nearer the shoulders as found by Hendrick (20), and Wood and Berry (19).

The other constituents determined are expressed as percentages of the dry matter, consequently a simple comparison of sampling methods from the percentage figures is not obtained. A better comparison is available from the results in table No. 60 giving total yields, although the simple manipulation required for dry matter determination with possibility of smaller

GRAPHS TO SHOW THE RELATIONSHIP BETWEEN AVERAGE CORE WEIGHTS (DIAGONAL CORING) AND PLOT YIELDS.



analysis error may be regarded as being in favour of dry matter figures as basis of comparison.

The yield figures for the constituents ash, Nitrogen, CaO, P_2O_5 show greatest variation by the different methods of sampling for plots Nos. 4 - 6 in CaO figures where sampling by quarter slices are consistently higher by about 10% than these from horizontal cores.

Relation between fresh core weights and plot yields.

Sansome (21) concluded that "the fresh weight of a core is a function of the weight of the whole root". It follows that in an experiment of this type where the number of bulbs in each plot is constant, the different yields being due to difference in size of the bulbs there should be a relationship between the average core weight and the total yield.

This relationship has been examined by comparing the average fresh core weight obtained by the diagonal coring method employed for plots No. 2 - 10 with the total yields. The relationship found is shown in the graphs opposite.

Table No. 61. Relation between fresh core weight and Yield of Bulbs.

Plot No.	Total Yield in tn/ac.	Fresh Core Average wt. in gm.
2	31.49	20.51
3	29.30	18.31
4	31.30	19.56
5	16.23	16.96
6	28.19	18.77
7	30.53	18.84
8	26.65	18.44
9	4.31	13.30
10	28.73	18.96

Difference in composition of bulbs due to fertiliser treatment.

The average figures for percentage dry matter and constituents according to treatment are tabulated in Table No. 62.

Table No. 62. Chemical composition of Swede bulbs according to fertiliser treatment.

Average results.

Treatment	% Dry Matter.	% Nitrogen	% Ash	% CaO	% P_2O_5
Untreated	10.27	1.97	4.425	.397	.294
Slag L.	9.65	1.655	4.505	.427	.513
Slag H.	9.68	1.72	4.66	.4455	.587
"Plot No.10"	9.89	1.90	5.36	.3864	.346

Discussion of results.

No increase in dry matter content has been obtained by the fertiliser treatments, it is however to be remembered that the bulbs from the untreated plots were smaller and the ratio of peripheral material to central flesh in the samples by the methods employed in such is larger than with the bulbs from the other plots. The nitrogen figures vary in a similar manner to the dry matter figures.

Percentage ash in highest in sample from Plot No. 10. Consideration of the other figures indicates that this is due to increased assimilation of some constituent, not determined. Treatment with slag H has increased the percentage of CaO and P_2O_5 in the dry matter to a significant extent. The P_2O_5 content in samples from slag H plots is double that of the control plot samples. The increase due to slag L is not so marked for % CaO. Such is to be expected from the low CaO content figure of the slag itself. The P_2O_5 content is not so great as for slag H treatment, but exceeds that of the untreated very appreciably.

Increases of yield of dry matter and constituents according to fertiliser treatment.

The mean yield of dry matter and constituents according to fertiliser treatment are given, expressed in lb. per acre in Table No. 63.

Table No. 63. Yields of dry matter and constituents according to fertiliser treatment.

Treatment	Dry Matter	Ash	Nitrogen	CaO	P_2O_5
Untreated	2368	108.2	47.5	9.74	7.23
Slag L	6498	292.7	107.7	27.69	33.35
Slag H	6298	294.1	108.3	28.27	37.06
"Plot No. 10"	6366	341.0	121.3	24.6	22.05

Increases, not apparent from the chemical composition figures, due to increased growth on the treated plots are shown. These are tabulated below - average results.

Table No. 64. Increases of dry matter and constituents according to treatment, lb. per acre.

Treatment	Dry Matter	Ash	Nitrogen	CaO	P_2O_5
Slag L	4130	184.5	60.2	17.95	26.12
Slag H	3930	185.9	60.8	18.53	29.83
"Plot No. 10"	3988	232.8	73.7	14.86	14.82
expressed as % of mean untreated plot yield.					
Slag L	174	170.5	127	184.3	361.3
Slag H	166	171.8	128	190.2	412.6
"Plot No. 10"	169	215.2	153	153	205

Discussion of Results.

The percentage increase in weight of bulbs is with Slag H 179%, Slag L 188% so that an increase in phosphate content where slag treatmant has been given is shown. With slag H a slight increase in calcium content has also resulted.

The other increases are due to the increased growth caused by the slag application.

The results for Plot No. 10 are tabulated for comparison, it is to be remembered, however, that they represent single plot determinations.

Comparison of the yield figures shows that, as in grassland experiment No. 1, the fertiliser values of the two slags are practically equal, under the conditions of the experiment. Slag L has given a slightly greater increase than slag H in bulbs and dry matter: while slag H has increased the P_2O_5 and the CaO yield slightly more than slag L.

The increases due to the slag treatment are however much greater than those of experiment No. 1.

The recovery figures for CaO and P_2O_5 contained in the slags:-

Slag H	CaO	2.63%	P_2O_5	13.27%
Slag L	CaO	3.7 %	P_2O_5	11.1 %

Field Experiment No. 3.

To test the residual value of the slags applied at Friarland Swede experiment in season 1933, on the out crop, Plots No. 1 - 9, were treated uniformly with sulphate of ammonia at the rate of ¾ cwt. per acre at the time of sowing, and 30% potash salts at the rate of 1½ cwt. per acre shortly after sowing.

The crop from the various plots was harvested separately and the total yield ascertained by weighing. After threshing the grain was weighed, the difference between total yields and grain weights was taken as straw yield. Details of the results obtained are given in the following Table No. 65.

Table No. 65. Plot yields - Friarland Oats, 1933.

Plot No.	Slag Treatment	Total yield (lb.)	Grain (lb.)	Straw (by difference) (lb.)
1	-	159	40.5) 98	118.5
2	L	181	57.5)	123.5
3	H	211	70.75	140.25
4	H	220	62.5	157.5
5	-	142	45.00	97.00
6	L	197	56.00	141.0
7	L	219	71.00	148.0
8	H	201	65.5	135.5
9	-	153	44.25	108.75

Grain yields for Plots No.1and 2 as given in Table 65 are not as found by weighing, grain from these plots was mixed on threshing and the total weight of grain from the two plots only was obtained. The results in the table were calculated from this weight.

The average plot yields according to fertiliser treatment are:-

Table No. 66. Plot yields according to fertiliser treatment.

lb. per plot.	Total yield	Grain	Straw
Untreated	151	43.25	107.75
Slag L	199	61.5	137.5
Slag H	211	66.25	144.75

Thus in second year following slag treatment an increase in total yield of about 30% of average unslagged plot yield is obtained.

As slight increase of yield due to slag H as compared with slag L is indicated by the mean figures of Table 66. This however is probably not significant as variations in individual plot yields as shown in Table No. 65 occur.

The "corner effect" shown in swede experiment by Plots 6, 8, and 9 is not in evidence here indicating that the soil deficiency as shown by crop yield has been remedied by the application of the other fertilisers.

Summary.

An experiment on poor grassland, with cutting of the herbage at different intervals during the growing season, under noted soil and weather conditions, to compare the effectiveness of two basic slags, as fertilisers, has been described.

A small recovery of the added CaO and P_2O_5 is noted but an increased content of these constituents in the herbage as compared with the product of the untreated soil has been obtained. An increase in the yield of Ash, Nitrogen, K_2O, and Na, has been brought about due to action of the slags in promoting increased growth.

The values of the slags as fertilisers under the conditions of the experiment are not in agreement with the availability of the P_2O_5 as indicated by the citric acid test.

A field experiment with swedes on a soil fairly representative of South Ayrshire has also been described. Marked increases in yield have been obtained by the application of a heavy dressing of the same two slags sown in the drill.

A comparison of different methods of sampling swede bulbs in the field has been made. The relation of fresh core weight and plot yields has been noted. Increased P_2O_5 content of the swedebulbs has been obtained by the slag treatment. One slag has given a slight increase in CaO also,

while the other of much lower CaO content has maintained the % CaO in the roots in spite of the greatly increased growth on the treated plots.

Large increases in yield of dry matter, ash, nitrogen, K_2O and Na due to increased growth caused by the slag applications have also been noted.

The effectiveness of the two slags as judged by the increased yields of roots and their constituents is practically equal and not in agreement with the citric acid solubility figures.

The residual values of the slags assessed by increased yields in grain and straw with the oat crop following the swedes have been found to be practically equal. An increased yield of about 30% that of the unslagged plots has been obtained.

Main conclusions formed are -

1. That the fertiliser values of the two open hearth basic slags, under consideration, as shown by the results of the field experiments described, are practically equal, and not in accordance with the availability of the P_2O_5 indicated by the citric acid test.

2. That the calcium compounds of such slags of so-called intermediate solubility are important as well as the phosphorus compounds. This is shown by the increased "CaO" and "P_2O_5" content of the herbage from plots treated with basic slag in Experiment No. 1., and by the maintenance of the "CaO" content of swede roots when a very large increase in yield has been obtained by the application of basic slag to the soil in Experiment No. 2 where increased "P_2O_5" content of the crop has also been obtained.

3. That fertiliser treatment with basic slags under the conditions described has resulted in increased yields of freshly cut herbage, dry matter, ash, "P_2O_5", "CaO", "K_2O", Na, N, from poor grassland, and of swede roots, dry matter, ash, CaO, P_2O_5, N, on arable land.

4. That slight variations in analytical results for swede "bulbs" occur according to the method employed in sampling.

5. That there is a relation between the average fresh core weight, for 50 cores taken diagonally, and the plot yield of swedes when the number of roots per plot is constant.

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A P P E N D I X.

Brief summary of analytical methods.

Slag Analysis.

The melt obtained with a fusion of finely powdered slag and a mixture of sodium and potassium carbonate in a platinum crucible is extracted with dilute hydrochloric acid. This solution is taken to dryness, and after a second treatment with hydrochloric acid the residue is baked at 120 C to dehydrate the silica.

Silica is filtered off (Whatmann No. 44 paper) after treatment of the residue with hot dilute hydrochloric acid dried, ignited and weighed as SiO_2.

The filtrate (1) from above is made up to a known volume, an aliquot of which is taken for the phosphate determination.

Phosphate. The phosphorus is precipitated as ammonium phosphomolybdate, which is separated by filtration and estimated volumetrically according to the modified Pemberton method (Richards and Godden - Analyst. Dec. 1924).

Iron and Aluminium - an aliquot of filtrate (1) is taken for these determinations. To the solution is added a known weight of ferrous ammonium sulphate sufficient to ensure

complete precipitation of the phosphate present. After oxidation with hydrogen peroxide, a separation is effected by the basic acetate method. (Quantitative Chem. Analysis - Clowes and Coleman - 13th Edit. p. 277). The basic acetate precipitates are dissolved in hot dilute hydrochloric acid, and the solution after cooling made up to a known volume. Half of this is treated with ammonium chloride and ammonium hydroxide solutions to precipitate the iron and aluminium as mixtures of hydroxide and phosphate. This is filtered off (Whatmann No. 41 paper), dried, ignited, oxidised with a few drops of nitric and sulphuric acids, reignited and weighed. Iron is estimated in the other half of the solution by titration with standard potassium dichromate, after reduction with stannous chloride. (Clowes and Coleman - Quan. Chem. Anal. 13th Edit. pp. 167, 277). From the above results the weight of aluminium is calculated by difference.

Iron-Ferrous is determined in a fresh portion of the sample of slag. (Clowes and Coleman, 13th Edit. pp. 163, 278).

Calcium is determined after removal of manganese (Clowes and Coleman 13th Edit. p. 278) in the filtrates from the basic acetate separation by precipitation with ammonium oxalate, followed by titration with standard potassium permanganate.

Magnesium. To the filtrate from the calcium determination is added some strong nitric acid. The solution is evaporated to dryness, and the residue ignited. This residue is dissolved in dilute hydrochloric acid solution and magnesium estimated as $Mg_2P_2O_7$ - (Clowes and Coleman 13th Edit. p. 89).

Manganese is determined colorimetrically in a separate aliquot of filtrate (1) after evaporation to dryness and treatment with syrupy phosphoric acid to decolourise the solution. (Yoe - Photometric Chem. Analysis, 1928. Vol.I, p. 273).

Sulphur is determined in a fresh portion of the sample by fusion with sodium carbonate and potassium nitrate. The sulphur is precipitated from the extract as barium sulphate (Clowes and Coleman 13th Edit. pp. 75, 79).

Soluble calcium oxide, silica, and phosphoric acid are determined by the methods outlined above after destruction of the organic matter, if necessary.

Soils. Sampling is carried out by cores to a depth of nine inches at a number of points to give a representative sample. This is transported to the laboratory where it is spread out

to dry at room temperature. When dry the soil is pounded in a wooden mortar and transferred to a 2 mm. sieve. The material failing to pass is rejected and subsequent analyses are made on the fine earth.

Mechanical Analysis is determined by the revised official method - (Agricultural Progress 1928, Vol.V).

PH Value is ascertained in water suspension by the quinhydrone method - soil : water ratio approximately 1 : 4, corresponding to the soil liquid ratio for determination of exchange acidity in the following determination.

"Lime requirement" is determined by the electrometric method of Hardy and Lewis (J. Agr. Sci. 1929, 19, 17) to final PH 7.0; and by Hutchison and McLennan's method (J. Agr. Sci. 1915, 7, 75). (Where lime requirement figures are given the method is indicated).

P_2O_5 HCl soluble. - The extraction is carried out according to the method adopted by the Agricultural Education Association (Agri. Progress, 1931, 8, 134). The acid liquid treated with fuming nitric acid to oxidise organic matter is taken to dryness and silica is separated. The P_2O_5 is determined by the volumetric method (as for phosphate in slags)

P_2O_5, citric soluble. - A quantity of 200 gm. of soil is shaken with 500 cc. 2% citric acid for 24 hours in an

end-over-end shaker. The solution is separated off, and a known volume taken for P_2O_5 determination by the method for HCl soluble P_2O_5.

P_2O_5 requirement of soil is determined by the method proposed by Kirsanov (Bull. Leningrad. Dept. Inst. Fert. Agro. Soil Sci. 1932, 38; C.A. 1932, 27).

Herbage. The freshly cut herbage is thoroughly mixed, and the approximate quantity required for determination of dry matter content is taken. Foreign matter is removed. This sample is "chopped". 50 gm. samples are weighed on aluminium trays. These are dried in the air oven at 80 °C until the difference between two successive weighings is less than .05 gm. The dried material is immediately ground to a fine powder which is stored in bottles with ground glass stoppers. Further determinations are made on this material.

Nitrogen is determined by the Kjeldahl-Gunning Arnold method. (official and tentative methods of analysis of the Association of Official Agr. Chemists 1930, 3rd. Edit. p. 21, Section 24).

Phosphorus is determined by the volumetric method used in the Rowett Institute. (W. Godden - Notes on analytical methods used in Biochemical Dept., Rowett Research Institute, Aberdeen, 1926).

Total Ash. A known weight is burned at a low red heat not exceeding dull redness, until free from carbon.

Insoluble Ash. Total ash is treated with hot dilute hydrochloric acid. The insoluble matter is filtered off, washed, dried, ignited, weighed and recorded as insoluble ash.

Soluble Ash is found by difference between total and insoluble ash.

The filtrate from the insoluble ash determination is made up to a known volume, aliquots of which are taken for CaO, K_2O and Na determinations.

CaO is determined by the volumetric method (Godden - Notes on Analytical Methods - Rowett Research Inst. Aberdeen 1926).

K_2O is determined by the volumetric cobaltinitrite method of Milne (J. Agri. Sci. 1929, 19, 541).

Na is determined by the method proposed by Blenkinsop (J. Agr. Sci. 1930, 20, 511).

Swedes - fresh cores or sectors according to the method of sampling are threaded together and weighed. These are air dried for a short time, then they are heated in the air oven at 75°C until constant in weight. The dried material in immediately ground in a Christy-Norris mill to a fine powder which is stored in bottles with ground glass stoppers. Determinations of Nitrogen, Ash, CaO, P_2O_5 are carried out by the methods used in herbage analyses.
